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High-pressure-shift freezing: Main factors implied in the phase transition time

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Abstract

We have studied the dynamics of the high-pressure-shift freezing (HPSF) process and the main parameters implied. Conventional freezing experiments at atmospheric conditions and HPSF experiments were carried out at identical temperatures and different pressures and the phase transition times compared. Phase transition times in HPSF experiments were lower than their homologues at atmospheric pressure in all cases. The reduction depends on the pressure and temperature conditions before expansion. These variables are highly involved in the supercooling reached and govern both the percentage of ice formed during the pressure release and the temperature drop in the pressure medium. After expansion, the pressure medium plays a significant role in the heat removal from the sample. Good predictions of plateau times can be made from initial pressure and temperature values, both process parameters that can be readily adjusted in the food industry.

Keywords: High-pressure; Freezing; High-pressure-shift freezing; Supercooling; Heat transfer

1. Introduction

Freezing can be defined as the crystallization of liquid water into its solid form, or ice. In order for freezing to occur, the temperature of the food must be below the corresponding freezing point. Heat must therefore be removed from the product to be frozen. However, crystallization is not automatic. A system may exist under thermodynamic conditions where the solid phase is the equilibrium phase, but this does not guarantee that the solid will be present. In many systems, it is possible—and indeed common—to have a supercooled liquid phase in a pressure-temperature combination in which ice is the thermodynamically stable phase (Reid, 2000). There are many factors involved in the tendency of a system to supercool, including temperature, rate of cooling, volume, type of container, particles in the liquid, etc. Even when all these factors are controlled, different extents of supercooling occur in repeated experiments (Heneghan, Wilson, & Haymet, 2002). The heterogeneous nucleation of supercooled water may thus be considered an unpredictable phenomenon. The probability of nucleation increases as the temperature decreases, and the nucleation rate also increases as supercooling increases (Reid, 1983). Burke, George, and Bryant (1975) found that for each degree (°C) of supercooling, the ice nucleation rate increased ca. 10-fold. Once supercooling ceases, phase transition occurs almost instantaneously throughout the supercooled zone. The latent heat is released and the temperature rises to the freezing point.

Charoenrein and Reid (1991) demonstrated the importance of the supercooling phenomenon and how it can be harnessed. In a study of ionic diffusion in starch gels, they compared the frozen structures produced by slow and rapid cooling. Surprisingly, slow cooling produced smaller, homogeneously distributed ice crystals.

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This was a consequence of supercooling of the whole gel cylinder under the experimental conditions that induced a uniform nucleation through the sample. These authors suggested a procedure to maximize the size of the supercooled zone by combining two consecutive cooling phases: first, slow cooling of the product to a temperature just above the nucleation temperature, allowing establishment of a large supercooled zone. The coolant temperature for this step must be set above the nucleation temperature. Once the large supercooling zone is established, the sample is transferred to a much colder heat transfer medium. Cooling reduces the surface temperature to below the nucleation temperature, initiating rapid freezing and a consequent reduction in ice crystal size.

Improvement of known freezing methods and development of new techniques (e.g., high-pressure freezing, dehydrofreezing, application of antifreeze and ice nucleation proteins) are important research objectives for the food industry (Li & Sun, 2001). In the last 10 years, high-pressure-shift freezing (HPSF) has become one of the most promising pressure applications for food preservation thanks to major advantages as regards product quality as compared to conventional methods. HPSF takes advantage of the phase diagram of water, introducing another mechanism to induce extensive supercooling. This involves instantaneous ice nucleation throughout the sample, with the formation of small ice crystals. The product to be frozen by HPSF is placed in a high-pressure vessel, previously tempered at the freezing temperature and immediately compressed. The sample is then cooled under pressure to a temperature close to its corresponding freezing point, but it remains unfrozen. Once this temperature is reached throughout the product, pressure is released either rapidly (in seconds) or slowly (in minutes) to produce different extents of supercooling, at atmospheric pressure or under pressure. This supercooling induces instant, uniform ice nucleation simultaneously throughout the sample. After expansion, crystal growth proceeds at atmospheric pressure, in order to increase the proportion of frozen water. It is generally accepted that no further nucleation occurs at this stage. High-pressure-shift freezing is particularly interesting because supercooling—and hence also ice nucleation—takes place just after pressure release; simultaneously throughout the product (as the pressure is applied isostatically) and not only on the surface as occurs in conventional freezing at atmospheric pressure. The extents of supercooling so attained induce high nucleation rates that promote the instantaneous crystallization of a percentage of water in the sample. Phase transition times (plateau times) are thus considerably reduced, and resulting ice crystals are granular-shaped and homogeneously distributed rather than typical dendritic structures (Martino, Otero, Sanz, & Zaritzky, 1998). Improvements in structure, texture and water holding capacity have been reported by many authors in different high-pressure-shift frozen products such as gels (Fuchigami & Teramoto, 1998; Kanda, Aoki, & Kosugi, 1992), vegetables (Koch, Seyderhelm, Wille, Kalichevsky, & Knorr, 1996; Otero, Solas, Sanz, de Elvira, & Carrasco, 1998) or meat products (Fernández-Martín, Otero, Solas, & Sanz, 2000; Martino et al., 1998). However, deteriorations in color, water holding capacity and texture of muscle tissues have also been described, depending on the level of applied pressure (Chevalier, Sentissi, Havet, & Le Bail, 2000; Fernández-Martín et al., 2000; Massaux, Berá, Steyer, Sindic, & Deroanne, 1999). Such changes have been attributed to myosin and actin denaturation under pressure.

Due to the advantages of this freezing method some attempts to model it have been made by different authors (Denys, Van Loey, Hendrickx, & Tobback, 1997; Sanz & Otero, 2000). Nevertheless, it is difficult to set parameters for the phenomenon of uniform nucleation induced by pressure release (Lévy, Dumay, Kolodziejczyk, & Cheftel, 1999). Various approaches (see Table 1) have been used to calculate the amount of ice instantaneously produced after expansion, some taking supercooling phenomena into account (Barry, Dumay, & Cheftel, 1998; Le Bail, Chourot, Barillot, & Lebas, 1997; Otero & Sanz, 2000) and others not (Chizhov & Nagornov, 1991; Otero, Sanz, de Elvira, & Carrasco, 1997). Also experimental measurements have been made

Table 1
Various approaches used to calculate the amount of ice instantaneously produced after adiabatic expansion in high-pressure shift freezing processes by different authors

Supercooling phenomena	Equation	Reference
Not taken into account	$\left(\frac{\mathrm{d}V}{\mathrm{d}p}\right)_S = m_i \cdot \left[(\frac{\partial V_i}{\partial p})_T + \cdot \frac{2 \cdot T_k}{L} \cdot (\frac{\partial V_i}{\partial T})_p \cdot (V_\mathrm{w} - V_i) - \frac{cp_i \cdot T_k}{L^2} \cdot (V_\mathrm{w} - V_i)^2\right] + (1 - m_i) \cdot \left[(\frac{\partial V_\mathrm{w}}{\partial p})_T + \frac{2 \cdot T_k}{L} \cdot (\frac{\partial V_\mathrm{w}}{\partial T})_p \cdot (V_\mathrm{w} - V_i) - \frac{cp_\mathrm{w} \cdot T_k}{L^2} \cdot (V_\mathrm{w} - V_i)^2\right]$	Chizhov and Nagornov (1991) Otero et al. (1997)
Taken into account	$m_\mathrm{w} \cdot cp_\mathrm{w} \cdot \Delta T_\mathrm{sup} = L \cdot m_i$	Le Bail et al. (1997)
Taken into account	$m_i \cdot L = [m_i \cdot cp_i \cdot \Delta T] + [(1-m_i) \cdot cp_\mathrm{w} \cdot \Delta T]$	Barry et al. (1998)
Taken into account	$\overline{cp}_\mathrm{w} \cdot \Delta T \cdot m_\mathrm{w} + \overline{cp}_i \cdot (1 - m_\mathrm{w}) = (1 - m_\mathrm{w}) \cdot T$	Otero and Sanz (2000)