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High-pressure calorimetric evaluation of ice crystal ratio formed by rapid depressurization during pressure-shift freezing of water and pork muscle

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Abstract

The amount of ice nuclei formed during the pressure release is important for the final formation and development of ice crystals in pressure shift freezing (PSF) frozen products. In this study, a high-pressure (HP) calorimeter was used to evaluate the ratio of ice crystals instantaneously formed by rapid depressurization during PSF of pure water and pork muscle tissue. Experiments were carried out initial pressure levels of 62, 115, 157 and 199 MPa, with corresponding phase change temperatures of −5, −10, −15 and −20 °C, respectively (slightly higher than phase change point of water–ice I). The ice crystal ratio was determined based on calorimetric peak measured and heat balance. The evaluated regression relationship between observed ice crystal ratio (R_{ice} in %) and pressure (P, MPa) was $R_{\text{ice–water}} = 0.115P + 0.00013P^2$ ($R^2 = 0.96$, $n = 9$) for pure water, and $R_{\text{ice–pork}} = 0.080P + 0.00012P^2$ ($R^2 = 0.95$, $n = 11$) for pork muscle. Compared to other methods, the calorimetric evaluation does not require any of the pressure-related properties of the test sample. HP calorimetry can thus be used to evaluate ice crystal ratio for PSF of foods even though their pressure related properties may be unknown.

Keywords: High pressure; Calorimetry; Pressure shift freezing; Ice-crystals; Pork

1. Introduction

Pressure shift freezing (PSF), as a new technique, is increasingly receiving attention in recent years because of its potential benefits for improving the quality of frozen food (Cheftel, Thiebaud, & Dumay, 2002; Le Bail, Chevalier, Mussa, & Ghoul, 2002). Based on the phase diagram of water under pressure (Bridgman, 1912), PSF process generally consists of three successive stages: (1) cooling the product to a subzero temperature under pressure (e.g., −20 °C at 200 MPa) without involving phase change; (2) followed by a quick depressurization (adiabatic expansion) to create super-cooling for instantaneous, uniform and partial initiation of the freezing process (resulting largely in ice nucleation); and (3) finally completion of the freezing process (ice crystal growth) at atmospheric pressure. PSF process has been demonstrated to produce fine and uniform ice crystals throughout the food samples (Chevalier, Le Bail, & Ghoul, 2000; Martino, Otero, Sanz, & Zaritzky, 1998), thus reducing ice-crystal related textural damage to frozen products (Chevalier, Sequeira-Munoz, Le Bail, Simpson, & Ghoul, 2001b; Otero, Martino, Zaritzky, Solas, & Sanz, 2000; Zhu, Le Bail, & Ramaswamy, 2003).

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Nomenclature

C_{Pice}	specific heat of ice (J g^{-1} °C^{-1})
$\overline{C}_{\mathrm{PfS}}$	mean specific heat of frozen sample (J g^{-1} °C^{-1})
K	ratio of heat flow rate to calorimetric signal (mW mV^{-1})
L	latent heat between water and ice at atmospheric pressure (333 J g^{-1})
m	sample mass (g)
m_{ice}	mass of ice instantaneously formed after pressure release (g)
P	pressure (MPa)
P_0	initial pressure before depressurization (MPa)
q	Heat flow rate (mW)
q_{b}	baseline of heat flow rate peak (mW)
Q	heat differential between sample and reference cells (J)
Q_P	adiabatic compression heat between sample and reference cells (J)
$R_{\mathrm{ice-pork}}$	ratio of ice crystal in pork instantaneously formed by pressure release (%)
$R_{\mathrm{ice-water}}$	ratio of ice crystal in water instantaneously formed by pressure release (%)
$R'_{\mathrm{ice-water}}$	ratio of ice crystal to water in test pork formed by pressure release (%)
S	calorimetric signal (mV)
t	time (s)
T	temperature (°C)
T_{f}	freezing temperature of water (°C)
V_{PR}	volume of pressure medium in reference cells (m^3)
V_{PS}	volume of pressure medium in sample cells (m^3)
Z_T	fraction of unfrozen water in frozen sample at temperature of T (dimensionless)
α	thermal expansion coefficient of pressure medium (K^{-1})

In the PSF process, after the pressure release, a portion of the liquid water is frozen and the resulting crystals are usually very small in size (like ice nuclei in conventional freezing) which will then grow when the freezing is completed at atmospheric pressure. Evaluation of the amount of ice nuclei formed instantaneously by depressurization is important for a better understand of PSF process. Three reasons are hypothesized for this: (1) the amount of ice nuclei initially formed determines the overall size, shape and location of ice crystals (the greater the number of ice crystals initially formed, the smaller is their size) (Zhu et al., 2003), thus reducing the extent of textural damage in frozen products; (2) the ratio of ice/water influences the thermal properties (conductivity, specific heat, etc.), of the water–ice mixture of the product (partially frozen) after depressurization, thus affecting final freezing behavior (Chizhov & Nagornov, 1991), and (3) it is necessary to determine the amount of ice nuclei formed for modeling of the process and estimate the time required to complete the freezing process (Otero & Sanz, 2003).

Several studies have been carried out on calculating the percentage of ice instantaneously formed after a quick depressurization (Barry, Dumay, & Cheftel, 1998; Chevalier, Le Bail, & Ghoul, 2001a; Le Bail, Chourot, Barillot, & Lebas, 1997; Otero & Sanz, 2000; Otero, Sanz, de Elvira, & Carrasco, 1997), as reviewed by Otero and Sanz (2003). In a study on deformation and flow of ice sheets, Chizhov and Nagornov (1991) proposed a thermodynamic model for the mixture of water and ice at subzero temperature under high pressure. The model was based on the phase-change curve of water–ice I (Bridgman, 1912), assuming that water always followed phase-change curve during expansion or pressurization. While in PSF process, pressure is always released rapidly so that liquid water always enters a super-cooled metastable condition before ice nucleation occurs (Knorr, Schlueter, & Heinz, 1998; Levy, Dumay, Kolodziejczyk, & Cheftel, 1999). Nevertheless, the above model has been used to predict ice amount produced after the expansion of pressurized water (Chevalier et al., 2001a; Otero et al., 1997).

Other calculation methods were based on heat balance between the latent heat released by ice nucleation and the sensible heat absorbed by the sample supercooled (Barry et al., 1998; Le Bail et al., 1997; Otero & Sanz, 2000). Le Bail et al. (1997) ignored the sensible heat of the ice initially formed and the negative adiabatic heat of the sample during pressure release. Barry et al. (1998) modified the heat balance by adding the sensible heat of the ice initially formed, but still ignoring the negative adiabatic heat of sample expansion. By directly using the model of Chizhov and Nagornov (1991), Otero et al. (2000) considered both sensible heat of the ice and the negative adiabatic heat after depressurization. However, they carried out the calculation using mean values of specific heat calculated at various temperatures (from minimum temperature reached after expansion to freezing point at atmospheric pressure). When the associated adiabatic heat effect is considered, the calculation will involve pressure-dependent thermoproperties that are not available for food materials. So