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Texture and structure of pressure-shift-frozen agar gel with high visco-elasticity

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Abstract

To determine the effects of sucrose and high-pressure-freezing, two kinds of agar gel were compared; A gel with high visco-elasticity and B gel, an ordinary dessert gel. Both agar gels with 0, 5, 10 or 20% sucrose were frozen at 0.1–686 MPa and -20 °C. They were frozen during pressurization, and exothermic peaks were detected at 0.1, 100, 600 and 686 MPa and -20 °C (freezing). However, at 200 MPa, they did not freeze but froze with released pressure (pressure-shift-freezing). Thus, the amount of syneresis from gel pressure-shift-frozen at 200 MPa was smaller than that from gel frozen at other pressures. Also, amount of syneresis from A was smaller than B. In addition, compared to control gels, the appearance of 0% sucrose–agar gels frozen at 0.1, 100, 600 and 686 MPa differed greatly due to syneresis and a volumetric shrinkage of the gel. It was apparent that the rupture stress of the gels decreased, strain and size of ice crystals increased and quality declined. Conversely, due to quick freezing, the texture and structure of both A and B pressure-shift-frozen at 200 MPa were better than the other pressure-treated gels and gels frozen in freezers (-20, -30 or -80 °C) at atmospheric pressure. Consequently, pressure-shift-freezing was more effective. However, texture, structure and syneresis of A were somewhat better than that of B. It was found that the addition of sucrose to the gel was effective in improving the quality of frozen agar gels.

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1. Introduction

Agar is a colloid extracted from seaweed (*Gelidiaceae* and *Gracilariaceae*), and currently used as a gelling, thicking and stabilizing additive (Armisen, 1999). In Japan, many kinds of dessert gel with agar have been used in traditional cooking. Recently produced in Japan are many kinds of agar powder having various textural properties (from soft to firm gel). In this paper, the freezing tolerance of two kinds of agar gel were compared; A gel with high visco-elasticity and B gel, an ordinary dessert gel discussed in the previous paper (Fuchigami & Teramoto, 2003b). The molecular weight of A is higher, about two times more than that of B. Also, the melting temperature of A is higher than

B, the texture (strength of gel) of A is softer than B and the amount of syneresis of A is smaller than B.

The main structure of agar is chemically characterized by repeating units of D-galactose and 3,6-anhydro-L-galactose with a few variations, and it has a low ester sulphate content. Agar is also a strongly gelling hydrocolloid. Typically, 1% agar is enough to make a rigid gel suitable for most applications (Matsuhashi, 1990). Thus, because of a high water content, damage to structures of agar gel through freezing is extensive. Agar gel, frozen by air blast method at atmospheric pressure, collapses and does not recover its gel phase when thawed, so texture after thawing becomes unacceptable. However, if high pressure is applied to frozen agar gel, the damage of gel may be prevented.

A non-freezing area (liquid phase) below 0 °C exists under high pressure (Fletcher, 1970; Hobbs, 1974). In previous studies (Kanda, Aoki, & Kosugi, 1992) when tofu was pressurized at 200 MPa and -18 °C, it did not freeze. However, when pressure was released, it froze quickly. This method was designated as 'pressure-shift-freezing'. Also, in previous studies (Fletcher, 1970; Hobbs, 1974) it was found

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that a specific volume of water increases during water-ice I transition, whereas the opposite is observed for 'high pressure ices' (II–IX). Ice I is less dense than liquid water and floats. The density of high pressure ices is higher.

In fact, the effect of high pressure on the improvement in quality (texture and structure) of frozen food has been discussed previously: tofu (Fuchigami, Ogawa, & Teramoto, 2002; Fuchigami & Teramoto, 1997; Fuchigami, Teramoto, & Ogawa, 1998; Kanda et al., 1992; Teramoto & Fuchigami, 1999); carrots (Fuchigami, Kato, & Teramoto, 1997; Fuchigami, Miyazaki, Kato, & Teramoto, 1997); Chinese cabbage (Fuchigami, Kato, & Teramoto, 1998); eggplant (Otero, Solas, & Sanz, 1998); potato (Knorr, Schlueter, & Heinz, 1998); emulsion (Levy, Dumay, Kolodziejczyk, & Cheftel, 1999); lobster (Chevalier, Sentissi, Havet, & Le Bail, 2000); konnyaku (Teramoto & Fuchigami, 2000); gellan gum gel (Fuchigami & Teramoto, 2003a); and agar gel (Fuchigami & Teramoto, 2003b). The results of these studies were as follows: pressure-shift-freezing at 200-400 MPa and -18 to -20 °C appeared to be effective in improving both the texture and/or histological structure of frozen food except for konnyaku (Teramoto & Fuchigami, 2000). When pressure-shift-frozen, nuclei formed during pressure release, and phase transition from liquid-to-ice I occurred quickly. Therefore, small ice crystals formed. Leading to a beneficial effect on texture. However, the effect of high pressure on improving the quality of frozen food appeared to be related to the type of food.

In a previous paper (Fuchigami & Teramoto, 2003b), changes in temperature and structure of agar gel, as affected by sucrose during high-pressure freezing, was investigated. Agar gel with 0, 5, 10 or 20% sucrose were frozen at 0.1–686 MPa and -20 °C. Exothermic peaks were detected at 0.1, 100, 500–686 MPa (freezing). However, at 200–400 MPa, gel did not freeze but froze during pressure release. Thus, structure of gel frozen at 200–400 MPa was better than other samples due to quick freezing. The phase transition from high-pressure-ices to ice I at -20 °C might have promoted the growth of ice crystals. With the addition of sucrose, the initial freezing temperature decreased and structural quality improved. However, changes in texture and syneresis during freezing-thawing were not discussed.

Therefore, the first objective was to determine the difference of texture between A and B during high pressure-freezing and conventional freezing at atmospheric pressure. The second objective was to determine the amount of syneresis from frozen-thawed gels. Finally, the third objective was to determine what affect addition of sucrose might have on the structure of A.

In this report, the freezing method of 100–686 MPa at -20 °C is referred to as high-pressure-freezing, although gel was not frozen at all these pressure levels. Also, the freezing method is designated as pressure-shift-freezing

when samples are cooled under pressure to -20 °C without ice formation then frozen when pressure is released.

2. Materials and methods

2.1. Sample preparation

Two kinds of agar powder, Yamato and Kanten Cook (Ina Food Co., Ina, Nagano, Japan) were used. Yamato-gel has a high visco-elasticity, while Kanten Cook is ordinary agar used for dessert gel. In this paper, Yamato and Kanten Cook are designated A and B, respectively. Samples were prepared as described previously (Fuchigami & Teramoto, 2003b). Agar powder was mixed with distilled and deionized water (1.5% w/w) for 10 min and heated to melting then boiled for 2 min to ensure the complete hydration of agar. Then, 0, 5, 10 or 20% (w/w) sucrose (saccharose, extra-pure reagent, Ishizu Seiyaku Ltd, Osaka, Japan) was added, and the mixture was heated for 2 min. After deairing for about 2 min using a vacuum pump, weight was adjusted using hot water, then the mixture was poured into plastic trays (gel thickness, 10 mm) and stored in a 5 °C refrigerator over night (about 20 h) to achieve complete stabilization. The gel samples were then cut into cylinders (15 mm in diameter and 10 mm height). Seven pieces of agar gel were vacuum packed in heat-sealed polyethylene bags. Four packs of samples with various concentrations of sucrose were frozen at the same time. These agar gel samples were designated as 0, 5, 10 or 20% sucrose-gel.

2.2. Method of freezing under high-pressure

High hydrostatic pressure treatments were carried out using a high-pressure food processor (Dr Chef, Kobe Steel Ltd, Kobe) as described previously (Fuchigami & Teramoto, 2003a,b; Kato, Teramoto, & Fuchigami, 1997). Propylene glycol, the pressure medium, was first placed in a pressure vessel (6 cm inside diameter and 20 cm high, surrounded with a jacket) and kept at -20 °C by a cooler (-35 to 10 °C) then removed. Next, samples were placed in a pressure vessel, and the thermocouple (k-type) was inserted in the center of the sample. The pressure medium $(-20 \,^{\circ}\text{C})$ was then added to the pressure vessel. Samples were immediately pressurized at 100-686 MPa. With the addition of the pressure medium, it took within 2 min to reach the defined pressure. The operation was fully automated and both pressure and temperature of the sample (upper section of the pressure vessel) and pressure medium (lower section) were recorded in intervals of 5 s using Thermodac E/Ef (Eto-denki Ltd, Tokyo).

After pressurization at 100, 200, 600 or 686 MPa and -20 °C for 63 min, pressure was released and gel samples were left for about 20 min in a pressure vessel to ensure

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