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Impacts of freezing and molecular size on structure, mechanical properties and recrystallization of freeze-thawed polysaccharide gels

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ABSTRACT

Freezing modifies microstructures and affects physico-chemical changes during thawing of foods. This study investigated impact of freezing temperature (−20 °C, −50 °C and −90 °C) and controlled freezing process, and dextrose equivalent (DE5, DE15 and DE18) of maltodextrin (MD) on microstructure, mechanical and structural changes (shrinkage and recrystallization) of freeze-thawed MD-agar gels. Shrinkage and turbidity of matrices were dependent on freezing conditions and microstructures of solids. X-ray tomography revealed that low cooling rate formed large ice crystals contributed to thicker solid networks. However, a slow cooling to a supercooled region (~0 °C to −1 °C) followed by a quench cooling caused rapid ice nucleation and inhibited ice growths resulting in only few clusters of large ice with a high number of fine ice crystals. Raman spectra indicated amorphous−crystalline transition (recrystallization) of gel components particularly maltodextrin after thawing in low DE systems which increased gel turbidity and subsequently accelerated shrinkage. Lower temperature freezing gave thinner but higher connectivity of solid networks providing higher mechanical strength and delayed recrystallization of maltodextrin which primary increased firmness values. The results indicated that the manipulation of freezing process in achieving small ice crystals effectively reduced structural changes attributing to recrystallization of high DE maltodextrin components in gel systems.

1. Introduction

Freezing is an excellent process to preserve food quality and develop new products i.e. frozen desserts. Ice morphology plays significant role in textural and physical properties of frozen foods. Size and location of ice crystals are keys in the quality of thawed products. Cooling rate is the most common variable controlling ice morphology in frozen and partly frozen systems (Petzold & Aguilera, 2009). Freezing affects microstructures and subsequent changes of food properties such as syneresis and drip loss in freeze-thawed tissues (Kidmose & Martens, 1999; Ngapo, Babare, Reynolds, & Mawson, 1999), texture and firmness of agriculture products (Kidmose & Martens, 1999; Miles, Morris, Orford & Ring; 1985; Sigurgisladottir, Ingvarsdottir, Torrissen, Cardinal, & Hafsteinsson, 2000; Badii & Howell, 2002) and increased toughness of meat (Badii & Howell, 2002) as well as accelerated protein denaturation (Benjakul, Visessanguan, Thongkaew, & Tanaka, 2003; Mackie, 1993; Tironi, Tomás, & Añón, 2010). The structural changes in frozen foods take place during freezing, storage and subsequent thawing. A rapid freezing forms small ice crystals and has been proved to reduce structural changes of frozen foods during storage and thawing. Accordingly, the controlled freezing condition to achieve small ice crystals is essential for frozen food industries. A faster cooling rate can be easily achieved by reduced freezing temperature in conventional freezer. In the present study, a control freezing protocol was used to achieve a rapid freezing after a slow cooling into the supercooled region below equilibrium freezing point.

The destabilization of food gels due to freezing such as drip loss

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and shrinkage significantly causes adverse effects to frozen products after thawing. Several studies indicated that freezing and thawing modify microstructures and accelerates retrogradation of starch gels (Charoenrein & Preechathammawong, 2010; Kim, Kim, & Shin, 1997; Lee, Baek, Cha, Park, & Lim, 2002; Muadklay & Charoenrein, 2008). The retrogradation of freeze-thawed starch gels led to the release of water adsorbed in the network of starch matrices or so called 'syneresis'. Consequently, the shrinkage of the gels occur as liquid drains from the pores of the matrices (Scherer, 1993). Addition of some food additives such as polysaccharides e.g. gums and maltodextrin has been proved to increase stability of some frozen products (Goff, 1995). Maltodextrin has wide food applications such as carrier for encapsulated components i.e. flavor and bioactive compounds, provide full-fat texture to reduced-fat formulations or fat replacer, modify structures for superior mouthfeel in frozen food and desserts with a lower cost (Chronakis, 1998; Gibbs, Kermasha, Alli, Catherine, & Mulligan, 1999; Setser & Racette, 1992). Previous study showed that various dextrose equivalent (DE) of maltodextrin controlled microstructure formation of freeze-dried matrices which attributed to the manipulation of unfrozen water and ice fraction (Harnkarnsujarit, Charoenrein, & Roos, 2012). Moreover, Rojas, Rosell, and de Barber (2001) showed that maltodextrins of low degree of polymerization (DP) and hence high DE effectively retarded staling of starch gels; however, lack of study revealed the effect of maltodextrin as well as their DE on structure properties of gel matrices after thawing. The structural changes of freeze-thawed systems which majorly contain maltodextrin and freezing effects have also rarely been investigated.

The amorphous starch component is thermodynamically non-equilibrium material and tends to recrystallize which can be measured by using various methods such as differential scanning calorimetry (DSC), X-ray diffraction, spectroscopic and turbidimetric methods (Karim, Norziah, & Seow, 2000). The DSC measures the energy required to disintegrate crystalline fraction relating to the degree of crystallinity which destroys the samples. While some other spectroscopic methods including infrared and Raman spectroscopy are non-destructive and can be used in on-line monitoring of structural changes of food products including retrogradation of amylose and amylopectin in starch components (Bulkin, Kwak, & Dea, 1987; Fechner, Wartewig, Kleinebudde, & Neubert, 2005; Li-Chan, 1996; Schuster, Ehmoser, Gapes, & Lendl, 2000). Raman spectroscopy is based on the distinct vibrational transitions that occur in the ground electronic state of molecules attributes to various stretching and bending deformation modes of individual chemical bonds (Li-Chan, 1996). The sample is radiated with a monochromatic visible or near infrared light from a laser giving the vibrational energy levels in the molecule to a short-lived, high-energy collision state. The activated molecules return to a lower energy state by emission of photon which has a lower frequency than the laser light. The difference between the frequency of the laser and that of the scattered photon is called the Raman shift given in reciprocal centimetres (Thygesen, Løkke, Micklander, & Engelsen, 2003).

The objectives of this study were to determine the effect of freezing on microstructure formations of maltodextrin-agar matrices and subsequent impacts on structural changes upon thawing. Moreover, the structural changes of freeze-thawed maltodextrin with various DE (DE5, DE15 and DE18) were investigated. Agar was formulated to form gel matrices mimicking semi-solid food structures. The findings give benefits to frozen food industry on manipulating freezing process and carbohydrate-based components in achieving highest food stability upon thawing.

2. Materials and methods

2.1. Maltodextrin-agar gels preparation

Maltodextrin (DE5, DE15 and DE18) and agar powders were purchased from Sigma–Aldrich Japan G.K. (Tokyo, Japan) and Wako Pure Chemical Co., Ltd. (Osaka, Japan), respectively. Solid mixtures (15 g/100 g) of maltodextirn-agar (9:1) were dispersed in distilled water (Water distillation apparatus RFD 240RA, Advantec®, Toyo Seisakusho Kaisha Ltd., Osaka, Japan). The maltodextrin-agar suspensions were stirred at 25 °C for 20 min using magnetic stirrer to allow for water adsorption of solids prior to heating to 90 °C and held for 5 min to ensure complete melting of agar. The mixtures were cooled, then poured into containers and left for gelation at 25 °C for 2 h.

2.2. Freezing and thawing

Gels containing maltodextrin were cut into 1-cm cubic and placed on aluminium trays prior to freezing. The freezing conditions composed of conventional chest freezers at −20 °C (dimension of 60 × 80 × 120 cm, SCR-R451G, Sanyo, Japan), −50 °C (dimension of 70 × 80 × 130 cm, Ultra Low, Sanyo, Japan) and −90 °C (dimension of 60 × 50 × 90 cm, MDF-C8v1, Sanyo, Japan) and three controlled freezing protocols using a program freezer (Taiyo Nippon Sanso Corporation, Tokyo, Japan) equipped with liquid nitrogen vessel. A pilot scale program freezer composed of a stainless steel freezing chamber (approximate dimension of 20 × 30 × 30 cm). The samples were loaded from the top with a metal scaffold and door was locked with metal clamps. A built-in temperature sensor was designed in the freezing chamber to monitor the temperature change and control the release of liquid nitrogen to the chamber during freezing. The programmed freezer is chamber temperature and time controlled to achieve target temperature. The freezer was programmed according to the trial experiments to control three freezing conditions namely protocol A, B and C. All the systems were programmed to prefreezing from 2 °C to target freezing temperature within a considered time followed by immediate cooled to −80 °C and held for 1 h prior to transfer to store in a chest freezer at −90 °C. The freezing profiles of each system are shown in Fig. 1. The gel temperatures during freezing were recorded at 1 s interval using type-T thermocouples (copper-constantan) connected to a data logger (Memory HiLOGGER LR8431, HIOKI E.E. Corporation, Nagano, Japan). The thermocouples (diameter 0.046 mm, response time <1 s, T-T40, Ishikawansangyo, Co. Ltd., Japan) were inserted to the center of the gels prior to freeze and attach to the aluminium plate with adhesive tape. The frozen gels were removed from the freezer and thawed at 25 °C under the ambient laboratory condition for 3 h prior to measure for mechanical properties and Raman spectra.

2.3. X-ray tomography

A Skyscan 1172 X-ray microcomputed tomography system (X-rayCT, Bruker, Kontich, Belgium) was used to measure the microstructures of freeze-dried solids which reflected ice formation in maltodextrin-agar systems. The frozen maltodextrin-agar systems were transferred to store at −90 °C for further 3 h prior to freeze-dry at below 100 Pa for approximately 60 h in a freeze-dryer (Kyowac, Kyowa Vacuum Engineering Co., Ltd., Tokyo, Japan). The vacuum was released with an ambient air. The freeze-dried solids were removed and stored in an evacuated desiccator containing P_2O_5 for 5 days to remove residual water prior to the measurement. The freeze-dried gels were wrapped with a cling film to prevent water adsorption and mounted on a rotational plate. The X-ray