Journal of Food Engineering 184 (2016) 10–20

Contents lists available at ScienceDirect

Journal of Food Engineering

journal homepage: www.elsevier.com/locate/jfoodeng

Effects of freezing on microstructure and rehydration properties of freeze-dried soybean curd

Nathdanai Harnkarnsujarit [a], [b], [*], Kiyoshi Kawai [c], Manabu Watanabe [a], Toru Suzuki [a]

[a] *Department of Food Science and Technology, Tokyo University of Marine Science and Technology, 4-5-7, Konan, Minato-ku, Tokyo, Japan*
[b] *Department of Packaging and Materials Technology, Faculty of Agro-Industry, Kasetsart University, 50 Ngam Wong Wan Rd, Lat Yao, Chatuchak, Bangkok 10900, Thailand*
[c] *Department of Biofunctional Science and Technology, Graduate School of Biosphere Science, Hiroshima University, 1-4-4 Kagamiyama, Higashi-Hiroshima, Hiroshima, Japan*

ARTICLE INFO

Article history:
Received 22 October 2015
Received in revised form
18 February 2016
Accepted 25 March 2016
Available online 30 March 2016

Keywords:
Freezing
Microstructure
Rehydration
Freeze-drying
Soybean curd

ABSTRACT

Ice crystallization controls the microstructure and subsequent mass transport of water in freeze-dried food matrices. This study investigated the effects of freezing on the microstructure and rehydration properties of porous, freeze-dried soybean curd. Soybean curd was prefrozen at various freezing conditions (−20 °C, −50 °C, −90 °C and in Liq.N_2) prior to freeze-drying. Scanning electron microscopy showed a correlation between pore morphologies and freezing temperatures. The patterns of ice formed in the 3-D matrices were revealed using X-ray computed tomography. The decreased freezing temperature from −20 °C to −90 °C gave clearer needle ice formation in parallel with heat transfer resulting in a sponge-like structure after rehydration with a corresponding wall thickness of 2.9–21.8 μm. Conversely, the Liq.N_2 freezing gave very fine ice crystals which effectively retained the fresh-soybean curd structure and color upon rehydration. Cracking increased with decreased freezing temperatures which also accelerated solid loss during rehydration. A correlation between the pore morphology (i.e. pore diameter and 1^{st}-order rehydration kinetics) was observed. Cluster analysis revealed that freezing at −20 °C and −50 °C changed the color; whereas, freezing at −90 °C and with Liq.N_2 effectively preserved the color of the rehydrated soybean curd. The results clearly demonstrated a process-structure-function relationship in freeze-drying which can be effectively utilized in the structural design of freeze-dried food materials.

1. Introduction

Food structure has a pronounced effect on the transport properties of foods (e.g., diffusivity, permeability and thermal conductivity). The physical structure of a food material is of fundamental importance in the developing field of food materials science (Krokida and Philippopoulos, 2005). The porous structures of dehydrated materials play a paramount role in the modeling of mass transfer applications in dehydrated foods (Marabi and Saguy, 2004). Food processing, such as freezing and dehydration, contribute to various structural changes of food matrices such as protein aggregation, phase separation of colloidal systems and the crystallization of water and solutes leading to the modification of functional properties, for example the stability of nutrients and hydration properties of freeze-dried matrices (Rhim et al., 2011; Harnkarnsujarit and Charoenrein, 2011; Voda et al., 2012). The microstructure of food is a key parameter in understanding food properties and stability.

The food model selected for the present study was soybean curd or tofu, which forms a gel as a result of the denaturation of soy protein. The principal components of soybean proteins are 11S (glycinin) and 7S (β-conglycinin). In their native state, soy proteins do not form a gel; therefore, the proteins are heat-denatured and then coagulated to form soybean curd with water, soy lipids and other constituents trapped in its gel network (Keshun, 1997). Proteins provide various functional properties of foods including water holding capacity; however, several food processes possibly modify and affect the functional properties of protein networks. Drying (including freeze-drying) potentially promotes protein aggregation

---

[*] Corresponding author. Department of Packaging and Materials Technology, Faculty of Agro-Industry, Kasetsart University, 50 Ngam Wong Wan Rd, Lat Yao, Chatuchak, Bangkok 10900, Thailand.
E-mail address: nathdanai.h@ku.ac.th (N. Harnkarnsujarit).

http://dx.doi.org/10.1016/j.jfoodeng.2016.03.014

(Wang et al., 2010) and therefore, possibly affects the functional properties of protein networks including their hydration characteristics.

Freeze-drying retains the high quality of foods and bioproducts including the appearance, nutrients, flavor and high rehydration capacity. The process consists mainly of freezing and dehydration under reduced pressure. The ice nucleation and growth during freezing directly impact the morphologies of the freeze-dried matrices (Petzold and Aguilera, 2009) namely pore size and membrane/network thickness. A successful freeze-drying process results in highly porous, dehydrated matrices with a high rehydration capacity, which is an important property of freeze-dried foods for consumption or used in various industrial applications such as instant soups and ready-to-eat products. The most important property of freeze-dried food products is the ability to properly rehydrate after liquid reconstitution using water or milk.

Rehydration is a process of moistening dry material, mostly, using abundant amounts of water, which causes adsorption of the water and leaching of solutes (Lewicki, 1998). Rapid rehydration with the least solid loss is required for a better quality of rehydrated products. Rehydration properties have been extensively investigated in plant materials, including fruits and vegetables (Krokida and Marinos-Kouris, 2003; Witrowa-Rajchert and Lewicki, 2006; Marques et al., 2009), while only a few studies have demonstrated the rehydration characteristics of protein-based food matrices (Babić et al., 2009).

The rates of reactions or the kinetic parameters describe how fast a reaction proceeds and are favored for the comparison of different factors. Numerous researchers have compared the kinetics of water uptake as influenced by food matrices due to different dehydration methods such as air-drying, freeze-drying and vacuum-drying (Farkas and Singh, 1991; Krokida and Marinos-Kouris, 2003; Witrowa-Rajchert and Lewicki, 2006; Marques et al., 2009) and dehydration processes (Lin et al., 1998; Marabi et al., 2004; Marabi and Saguy, 2004; Babić et al., 2009; Rhim et al., 2011; Voda et al., 2012). However, very limited research has focused on the influence of varying the freezing process on the kinetics of water uptake of freeze-dried matrices. In addition, the previously reported data about the influence of the freezing process on the rehydration properties of freeze-dried foods are inconsistent (Farkas and Singh, 1991; Kuprianoff, 1962; Babić et al., 2009; Rhim et al., 2011; Voda et al., 2012). Rhim et al. (2011) reported that freeze-dried rice porridge frozen at −5 °C absorbed water most rapidly, followed by −20 °C, −70 °C and −40 °C, respectively. Generally, the rehydration ratio increased with an increase in the freezing temperature except for freezing at −40 °C which was probably due to the prolonged time for ice crystal formation and the slow freezing rate in the −40 °C system (Rhim et al., 2011). Kuprianoff (1962) and Babić et al. (2009) demonstrated that slow-frozen samples had higher rehydration percentages than fast-frozen samples due to larger holes. These aforementioned authors suggested that large ice crystals formed by slow freezing were preferable in the freeze-drying process since they promoted the reconstitution of the freeze-dried products. Conversely, Farkas and Singh (1991) reported that slower freezing caused poorer rehydration in freeze-dried, white chicken meat which was possibly due to the aggregation of muscle protein, especially cross-linking of actomyosin. Accordingly, contradictory conclusions regarding the freezing effects on the rehydration capacity of freeze-dried foods were found based on these previous investigations.

The objective of this study was to determine the effects of freezing conditions on microstructure and their subsequent impacts on the rehydration properties including the kinetics of water uptake, solid leaching, microstructural properties and surface color of freeze-dried, soybean curd matrices. Various freezing conditions, namely at −20 °C, −50 °C, −90 °C and in liquid nitrogen (Liq.N_2), were applied to control the microstructural properties of the solids. This study emphasized the importance of the process-structure-function relationship in freeze-dried systems and would be beneficial in the design structures of freeze-dried food matrices for desirable rehydration properties.

2. Materials and methods

2.1. Freezing and freeze-drying

Soybean curds or tofu (10 × 10 × 3 cm) were purchased in the same lot from a local market in Tokyo (moisture content 88.67% w.b.). The soybean curd samples were cut into 15 × 15 × 5 mm. Approximately 100 pieces of samples were placed between two aluminum trays (approximately 15 × 22 × 2.5 cm) prior to prefreezing in conventional freezers at −20 °C, −50 °C and −90 °C for 20 h as well as using liquid nitrogen freezing. The liquid nitrogen freezing was performed by placing the aluminum trays and samples in a polystyrene foam box. The liquid nitrogen was poured into the bottom of the foam box as well as on the upper trays to freeze the soybean curd for 15 min which was then transferred to storage at −90 °C. The freezing profiles of the soybean curd samples were recorded at 0.1 s intervals using type-T thermocouples (copper-constantan) connected to a data logger (Memory HiLOGGER LR8431, HIOKI E.E. Corporation, Nagano, Japan). The thermocouples were inserted at the core of the tofu samples and placed at identical distances between the aluminum plates. The freezing properties as shown in Table 1 were calculated from triplicate samples. After prefreezing, all soybean curd samples were transferred to storage at −90 °C for 24 h prior to freeze-drying. The frozen soybean curd samples were freeze-dried at below 100 Pa with a step-increased, shelf-temperature of 5 °C every 6 h from −40 °C to 20 °C using a freeze-dryer (Kyowac, Kyowa Vacuum Engineering Co., Ltd., Tokyo, Japan). The vacuum was released with ambient air. The freeze-dried samples were stored in an evacuated desiccator containing P_2O_5 to remove residual water prior to the measurement and considered as having “zero” water content.

2.2. Scanning electron microscopy

Microstructural properties of freeze-dried materials were measured using a scanning electron microscope (FEI Quanta-250 SEM, FEI Company, Czech Republic). Freeze-dried soybean curd samples were sectioned with a sharp blade and placed on the SEM stub using two-sided, adhesive carbon tape prior to sputter-coating with platinum using an E-1030 ion sputter (Hitachi Science Systems, Ltd., Japan). The specimens were transferred to the SEM and the images were collected under low vacuum (100Pa) at a 10 kV accelerated voltage and spot size of 6.0 with a large field detector (LFD). The SEM images were captured at 100× magnification.

The SEM images were analyzed for image pixels which were further converted to a physical size using the scale bar of the SEM micrographs. The pore diameter and wall thickness of freeze-dried soybean curd were randomly evaluated from 23 areas of each image. The average length of the maximum and minimum diameter in each pore was determined as the pore diameter and the wall thickness was measured as the distance between two pores.

The wall thickness of the freeze-dried matrices was derived as described by Harnkarnsujarit et al. (2012) with an assumption of the formation of spherical ice crystals to derive the number of ice crystals formed at the maximum freeze-concentration of the systems that was maintained throughout freeze-drying. This presumed freezing of water to form an unfrozen phase with 80% solutes and 20% water (Roos and Karel, 1991; Roos, 1993) An