Effect of supercooled freezing methods on ice structure observed by X-ray CT

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ABSTRACT

Because the quality of frozen food depends on the size of ice crystals, many studies have investigated the growth mechanisms of ice crystals in frozen foods. Recently, we developed a novel freezing method called the “supercooled freezing method” to better understand the detailed mechanisms for the growth of ice crystals. In this study, X-ray micro tomography was used to investigate the 3D structures of ice crystals in soybean curds that were frozen by the supercooled freezing method (Skyscan1172, Bruker microCT, Belgium). The 3D ice crystal structure produced by the conventional freezing method was also measured for comparison. In addition, the 3D structure of ice that occurred at different degree of supercooling was also investigated. The results revealed that the conventional freezing method formed cylindrical ice crystals and inhomogeneous configurations, whereas a high degree of supercooling created spherical ice crystals and relatively homogenous configurations. Further, a higher degree of supercooling produced more spherical ice crystals at a lower volume rate. Therefore, the supercooled freezing methods produced similar homogenous ice formation in the 3D structure to that previously found during experiments with pressure-shift freezing.

1. INTRODUCTION

Freezing is one of the best methods for food preservation that can extend the shelf life of food. However, food quality such as texture, color, and water holding capacity decreases because of the formation of ice crystals during the freezing process. Because the quality of frozen food depends on the size and location of ice crystals, numerous studies have been conducted to prevent the growth of ice crystals. The rapid freezing rate, predehydration treatment, antifreezing protein, and pressure has been extensively researched. Recently, it was found that in the typical freezing process, the finer ice crystals formed in soybean curd with large-scaled supercooling incidentally occurred during the cooling process compared with that formed by freezing without supercooling at the same cooling rate.[1)] In addition, it was reported the freezing with supercooling not only forms fine ice crystals but also possesses homogenous structures.[2)] In current study, our group therefore applied this phenomena as a novel freezing method, to consider the effects of freezing with supercooling (referred to as “supercooled freezing method or supercooled freezing,” hereafter) on the quality of frozen model foods. In particular, soybean curd was used as a food model for this experiment to characterize the size and shape of ice crystals, including the drip and fracture stress after thawing. The results of supercooled freeing method were compared with it of conventional rapid freezing methods. These results revealed that the supercooled freezing method provided smaller amounts of drip loss and lower fracture stress than the conventional rapid freezing method. This suggests that supercooled freezing has the potential to improve the quality of the frozen food.[3)] However, in the core of the samples, the crystal size of the supercooled freezing sample was larger than that of the conventional rapid freezing sample. Additionally, shapes of the ice crystals were not vastly different in both freezing methods. These results of ice morphology in this our previous work contradicted the result of others previous work such as the Miyawaki’s study and the Shimoyamada’s study[1)2)]. In fact, our previous study has based on 2D cross-sectional microscopic images of the frozen samples, which illustrated the information in a narrow view. The former observation method made it difficult to understand complex ice morphology such as the shapes and the size distribution of the ice crystals. 3D observations by X-ray CT can provide the structural information from the wide viewing field and allow further understanding of the growth mechanism in the ice crystals. Therefore, in this study, the 3D structures of ice crystals in the soybean curds which were frozen with the supercooled freezing method and conventional freezing method were investigated by X-ray micro tomography Furthermore, the ice crystal structures that were crystallized at different temperatures in the supercooled freezing method were also measured, and the effects of crystallization temperature on the ice structure were investigated.

2. EXPERIMENTAL PROCEDURE

In this study, two series of experiments were conducted. The first one (experiment 1) compared supercooled and conventional freezing, whereas the second one (experiment 2) disclosed the effects of the degree of supercooling on frozen food quality. The series of experiments used different types of soy bean curd manufacture, size of samples and freezing process as described below.

2.1. Sample preparation

In experiment 1, soy bean curds manufactured by Satonouki shokuhin Co., Ltd. were used as samples and were cut into 2 cm cubes, and a thermocouple was inserted into the center of the curds. In experiment 2, long-shelf life soy bean curds manufactured by Morinaga Co., Ltd were used as samples. The soy bean curds were cut into 1.5 cm cubes and frozen with thermocouples.

2.2. Freezing method

In both experiments, while the curds were in the freezing process, the temperature was recorded, and a real time freezing curve was drawn. Supercooling the samples in experiment 1 was achieved by cooling the samples very slowly at −5°C for 1.5 h. The air temperature in the chamber continued to decrease to −10°C with a rate of −2°C/h. In this method, some samples reached the supercooling state. Subsequently, its supercooling state was spontaneously released and resulted in ice nucleation. After the ice was nucleated, the air temperature in the chamber immediately changed to −80°C and the freezing process was complete. Conventional rapid freezing samples were produced by freezing soy bean curds in air blast freezer. In addition, the soy bean curds that did not achieve a supercooling state but went through the supercooling method were considered conventional slow freezing samples. Experiment 2 utilized two methods to cool the samples which had various nucleation temperatures in the supercooled freezing process. In one method, samples were cooled to −5°C in a chamber that cooled the air at a rate of −10°C/h. Subsequently, the samples were cooled to −40°C in a chamber that cooled the air at a rate of −60°C/h. In the other method, the samples were kept at 12°C at first and then cooled to −40°C in a chamber that cooled the air at a rate of −60°C/h. At this time, the ice crystallization temperature caught up with that of the freezing curve.

2.3. Measurement of ice structure by X-ray CT

We observed the ice crystal structures, in the soy bean curds by X-ray CT following Mousavi's method.[4] The frozen soy bean curds were freeze-dried so that the ice crystals could be sublimated inside. The 3D structures of the remaining pores were then scanned by an X-ray micro CT and were considered to represent the ice crystal structure. Scans were performed with a Skyscan1172 at 55 keV and 100 μA, with a pixel size of 10.8 μm or 5.0 μm. Reconstruction software from the resultant radio-transmission image was used to obtain cross-sectional images which were analyzed with image analyzing software that determined the area values and equivalent circle diameters of the ice crystals. In experiment 2, the cross-sectional images were used to obtain the 3D structures of the ice crystals. The volume rates for the ice crystals in the soy bean curds were also calculated.

3. RESULTS AND DISCUSSION

3.1. Experiment 1: Effect of the freezing method on the structure of ice crystals

Figure 1.1 illustrates the freezing curves of three kinds of freezing. These were measured at the core of the sample. This figure shows that supercooling did not occur in both samples of conventional freezing methods. The supercooled freezing method samples were maintained the supercooling state up to −10.6°C and ice crystallization occurred at the temperature. Figure 1.2 illustrates the freezing curve obtained from the supercooled freezing method, particularly the temperature hysteresis of supercooling state burned and ice crystals were formed.

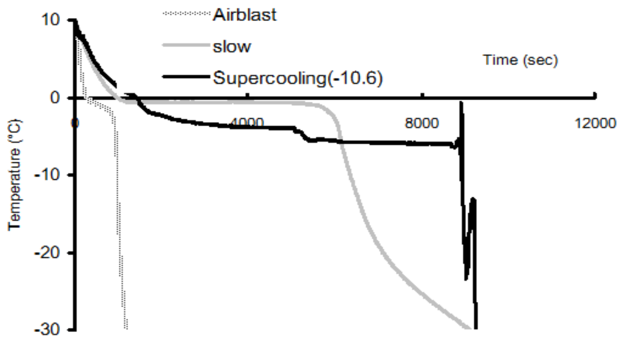

Fig.1.1 Freezing curves from the different freezing methods

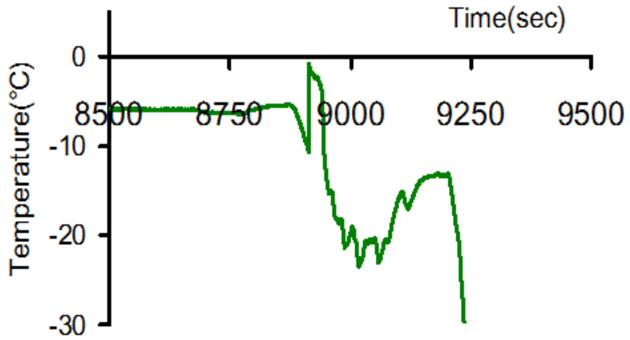

Fig.1.2 Freezing curves obtained from the the supercooled freezing method

Figure 2 shows the reconstructed cross-sectional images of the soy bean curds that were frozen by different freezing methods. Figure 2(a) shows that the ice crystals, which were formed from the conventional rapid freezing methods, were small and slit-shaped. They grew from the surface towards the center of the soy bean curds; however, few ice crystals were observed at the core of this sample.

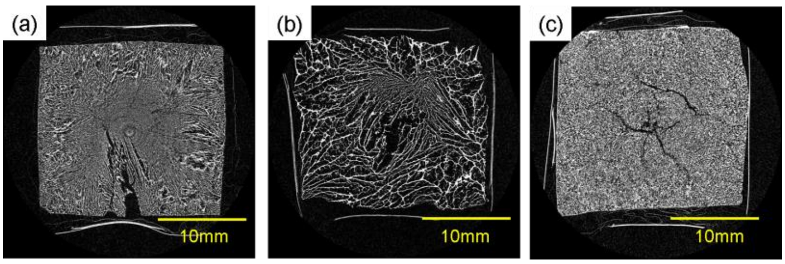

Fig.2 Cross-sectional images of the soy bean curds that were frozen by (a) the rapid freezing method, (b) the slow freezing method, and the (c) supercooled freezing method

Figure 2(b) shows that the slow freezing method caused the formation of large ice crystals. These sizes were larger than the size of ice crystals from the rapid freezing method [Fig. 2(a)], but both methods produced ice crystals with similar shapes. In contrast, the ice crystals in Figure 2(c) were formed by the supercooled freezing method and were spherically shaped and small in size. Their size did not depend on the location of the crystallized ice. Therefore, the ice crystals formed by the supercooled freezing method were spherically shaped and had a homogenous structure. However, the size of the ice crystals in Figure 2(a) and 2(b) depended on the location of the crystallized ice in the sample.

3.2. Experiment 2: Effect of nucleation temperature on the ice structure formed by the supercooled freezing method

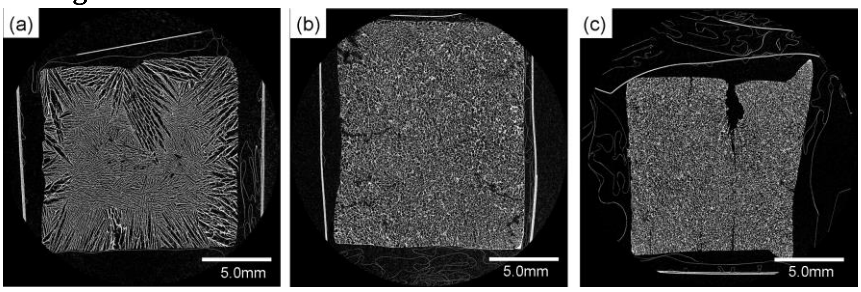

Fig.3 Cross-sectional images of the soy bean curds frozen by the supercooled freezing method. Ice crystallized at (a) −1.8 °C, (b) −4.5 °C, and (c) −7.5°C

Figure 3 shows the reconstructed cross-sectional images of the soy bean curds that were frozen by the supercooled freezing method. The ice was crystallized at different temperatures. Figures 3(a), 3(b), and 3(c) show the ice crystallized at −1.8°C, −4.5 °C, and −7.5°C, respectively. These pictures revealed that lower crystallization temperatures resulted in finer and spherical ice crystals. Furthermore, lower crystallization temperature resulted in more homogenous crystal configuration

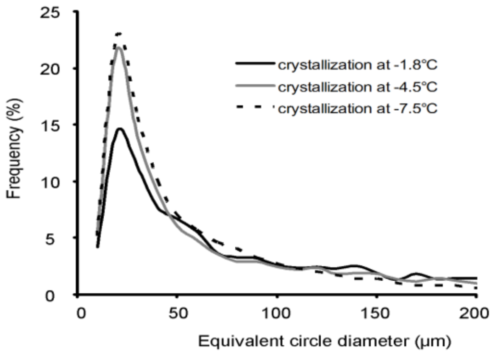

Fig.4 The distribution curve of the equivalent circle diameter of ice crystals that were frozen with the supercooled freezing method

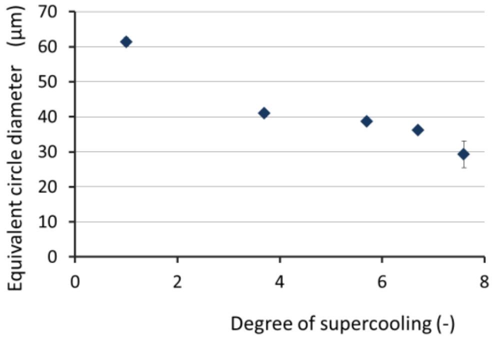

Fig.5 The equivalent circle diameter of ice crystals that were frozen with the supercooled freezing method at different degrees of supercooling

Figure 4 shows the distribution curve of the equivalent circle diameter of ice crystals which were calculated from the cross-sectional images. The peaks for all the samples were observed between 10 and 50 μm. However, the distribution of the ice crystals formed at −1.8°C was broader than that of the other samples that had sharper distributions. These distributions are reflected in the configuration of the ice crystals, such that the broader distribution was less homogeneous, whereas the sharpest one was the most homogenous.

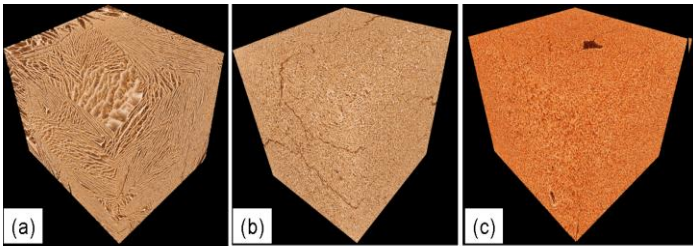

Fig.6 The 3D images of the soy bean curds frozen by the supercooled freezing method. Ice crystallized at (a) −1.8 °C, (b) −4.5 °C, and (c) −7.5°C

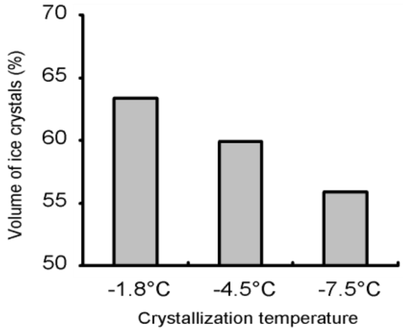

Fig.7 Volume of ice crystals frozen by the supercooled freezing method at different crystallization temperatures

In addition, Figure 5 shows the equivalent circle diameter of the ice crystals that were frozen at different crystallization temperatures. The size of the ice crystals was a function of the crystallization temperature, and lower temperatures of ice crystallization formed smaller ice crystals. Figures 6 and 7 show the 3D images of the ice crystals and the volume of the ice crystals, respectively. Figure 6(a) was significantly different from Figures 6(b) and 6(c).Figure 6(a) shows its porous structure and the volume of ice crystals in this sample was highest, as shown in Figure 7. While the 3D images in Figure 6(b) and 6(c) appeared similar, the volume of their ice crystals depended on the crystallization temperature.

4. CONCLUSIONS

The difference of distribution in size and shapes of the ice the crystals between the conventional freezing method and supercooled freezing method could be investigated with an X-ray CT. Crystallization temperatures in the supercooled freezing method affected the distribution of the size and shapes of the ice crystals. The difference of the ice structures by the supercooled freezing method was attributed to the difference in the sites where nucleation occurred. In the conventional freezing method, ice nucleation mainly occurred at the surface of the sample. Therefore, the ice crystals grew linearly in cylindrical shapes and were inhomogeneous structures. In the supercooled freezing methods, ice nucleation occurred at the surface and at the center of the samples; therefore, the ice crystals grew in every direction, spherically, and were homogenous structures. Furthermore, the ice crystallization temperature affected the character of the ice structures, which was because of the amount of nuclei that was crystallized at a specific degree of supercooling. Previous studies on pressure shift freezing revealed that after the pressure was released, the degree of supercooling affects the size of ice crystals.[5, 6)] In this study, the size, shapes, and distribution of ice were investigated, and the results showed that these characteristics were affected by the crystallization temperature. However, this study focused only on the freezing process; further experiments are needed to investigate the storage effects on the ice crystals that were formed by supercooled freezing method during storage period. During storage period, even at the isothermal condition, the size and the number of ice crystals is changed by Ostwald ripening. Therefore it should be investigated whether the specific character of ice crystals formed by supercooled freezing method can be kept or not. In addition, future studies should examine whether the supercooled freezing method improves the quality of real frozen foods such as meat, fish, and vegetables. Therefore, we will continue further research on the supercooled freezing method.

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