Recrystallization behavior of ice crystals in sugar-based solutions

[課程博士・論文博士共通]

博士学位論文内容要旨
Abstract

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論文題目 Title	Recrystallization behavior of ice crystals in sugar-based solutions (糖系溶液中の氷結晶の再結晶化挙動に関する研究)		

Freezing process is widely used method to preserve food in long term storage. During storage and distribution, an increase in the mean size of ice crystals by recrystallization is a major difficulty leading to quality deterioration such as the damage of cell structure in meat causing drip loss, an icy texture of ice cream. Recrystallization is defined as any change in the size, shape, orientation, or perfection of individual crystals after the completion of solidification. Three recrystallization mechanisms occur in frozen system under constant temperature conditions; accretion, migratory, and isomass recrystallization. Accretion recrystallization is the process by which two or more ice crystals contacting each other merge into one larger crystal by bridging between their surfaces. It is the major recrystallization mechanism affecting early stages of recrystallization. The major recrystallization mechanism at the later process is migratory recrystallization. It is the process by which larger crystals grow in a polycrystal system at the expense of smaller crystals. The water molecules on the surfaces of smaller crystals tend to migrate to the surfaces of larger ice crystals because of their higher specific surface energy. Consequently, the larger ice crystals grow while smaller crystals disappear. Isomass recrystallization is the process by which the rough surface of a single crystal becomes smoother by the surface energy minimization principle. It has been recognized that the recrystallization of ice crystal is an important phenomenon that must be controlled to increase the quality of frozen food. However, only limited number of ice recrystallization rate constant data are available until now and systematic studies of recrystallization of ice crystals have been hardly carried out. Sugar-based solution containing various di- and trisaccharides, polysaccharides and protein can represent simple model food. In this research, the recrystallization of ice crystals in these solutions were investigated to reveal the effect of these component upon recrystallization behavior for systematic understanding of ice recrystallization in frozen foods. Simultaneously, properties of freeze-concentrated matrix were also estimated by dielectric relaxation spectroscopy, NMR, fluorescent microscopy and differential scanning calorimetry (DSC) to understand the mechanism causing the effects. The research was divided in four parts; (1) Correlation between ice recrystallization rate and dielectric relaxation time in the series of saccharide solutions, (2) Ice recrystallization in sucrose, trehalose and raffinose solutions, (3) Ice recrystallization in sucrose solution containing polysaccharide (xanthan gum and locust bean gum), and (4) Ice recrystallization in sucrose solution containing protein (bovine serum albumin; BSA). In general introduction part; the background, purpose, and importance of this research as described above were stated.

In Chapter 1, literature review about water freezing, recrystallization of ice crystals, and the experimental techniques used for estimating molecular mobility was carried out.

In Chapter 2, the dielectric relaxation spectroscopy of series of mono and disaccharide solutions (maltose, sucrose, glucose, and fructose) were investigated and the correlation between the dielectric relaxation time in freeze-concentrated matrix and the ice recrystallization rate constant in these solutions were examined. A broadening of the dielectric relaxation function was described well by double Cole-Cole functions and two dielectric relaxation time were obtained. The fast relaxation time was assigned as that of free water. The difference in ice recrystallization rate can be explained well by the difference of dielectric relaxation time of free water in freeze-concentrated matrix even though the combination effect of solutions such as types of sugars, temperatures and concentrations. These results suggested that the dielectric relaxation time of free water was a useful parameter to predict and control recrystallization rate of ice crystals.

In Chapter 3, the recrystallization behavior of ice crystals in trehalose and mixture of trehalose and raffinose solutions were investigated at -5, -7, and -10 °C. These saccharides have been expected as an ingredient for frozen

food because of their unique characteristics, such as less sweetness, cryoprotective actions, and physiological functions. However, understanding the recrystallization behavior of ice crystals in the presence of these saccharides have not been extensively studied until now. The recrystallization rate constant of trehalose solution tended to be smaller than those of sucrose at the same temperature. The mixture solution of trehalose and raffinose retarded ice recrystallization only at -5 ºC and -7 ºC. The recrystallization rate constant of ice crystals was correlated well with the dielectric relaxation time of free water in a linear fashion. The correlation between ^{1}H spin-spin relaxation time T_2 of water component in freeze-concentrated matrix and the recrystallization rate constant was also fairly reasonable. These results suggested that difference of recrystallization rate constants among trehalose, sucrose, and mixture of trehalose and raffinose solutions were caused by difference of mobility of water molecules in freeze-concentrated matrix. That is to say, the observed trend of smaller recrystallization rate constants in trehalose solution and mixture solution of trehalose and raffinose were originated from smaller water mobility in freeze-concentrated matrix of these solutions.

Polysaccharides are also important components which are widely used in frozen food especially in ice-cream. However, the knowledge of polysaccharide ability to retard ice recrystallization was not clear until now. In Chapter 4, the recrystallization behavior of ice crystals in sucrose solution containing polysaccharide were investigated by using locust bean gum (LBG) or xanthan gum (XG) as a model polysaccharide. Increasing polysaccharide concentration did not always give smaller recrystallization rate constant of ice crystals. The trend of larger recrystallization rate constant was observed in the sample containing xanthan. The fluorescent microscopy showed that inhomogeneous distribution of xanthan in freeze-concentrated matrix, indicating phase separation by cryogelation during freezing process. From these observation, the following mechanism causing larger recrystallization rate constant may be possible; sucrose molecules were entrapped in the cryogel matrix during initial freezing process. As the result, apparent freezable water content increased and then recrystallization rate constant increased. These mechanisms can be supported by the heterogeneity of water mobility from the shape of dielectric relaxation spectrum curves.

In Chapter 5, the effect of protein addition on the recrystallization rate constant of ice crystals in 20% sucrose solution was investigated by using bovine serum albumin (BSA) as a model protein. Protein is one of important component in food. However, there have been few researches about the ice crystal recrystallization behavior in the presence of protein. Increasing BSA concentration (0 to 6%) reduced freezable water content in the samples. The size of ice crystals decreased with increasing BSA concentration, which can be explained by the reduced freezable water content. However, recrystallization rate constants of all samples were not significantly different. The dielectric relaxation time of free water did not change by increasing BSA concentration from 0 to 4% but in the presence of 6% BSA it took smaller value. This may be caused by loosely bound water in the outer of hydration shell of BSA.

In conclusion, we have demonstrated that the dielectric relaxation measurement was a useful tool to obtain the parameter for predicting and controlling recrystallization rate constant of ice crystals. Furthermore, the effects of existence of basic food components (di and trisaccharides, polysaccharides, and protein) on ice recrystallization rate constant were experimentally revealed and some of the mechanisms causing these effects were also successfully proposed. The results obtained in this study would be helpful to understand, predict and control the recrystallization behavior of ice crystals in frozen foods in a systematic way.