Ice recrystallization behavior of starch-based system

[課程博士・論文博士共通]

博士学位論文内容要旨
Abstract

専　攻 Major	Applied Marine Biosciences	氏　名 Name	Kamrunnaher Monalisa
論文題目 Title	Ice recrystallization behavior of starch-based system		

In recent decades, the demand for frozen ready meals has expanded significantly in food markets. During freezing the moisture content in the food turns to ice, and over time the ice crystal size, number, and distribution change due to a process known as ice recrystallization. By disrupting microstructure and texture, this phenomenon causes quality deterioration of the frozen product. Two basic processes can cause ice to recrystallize at a constant temperature. The first is migratory recrystallization, which results in the formation of large ice crystals by removing water molecules from small ones, and the second is accretions, which occur when two independent ice crystals are merged and sintered together. Recrystallization of ice crystals is an undesirable phenomenon that must be controlled to improve the quality of frozen food. Although some preceding research reported the effect of hydrocolloids and gums on ice recrystallization however systematic studies of ice recrystallization behavior of the starch-based system have rarely been reported. Starch is a complex food-grade biopolymer. It has been used as an additive or as the primary raw material in wide variety of frozen foods (soups, sauces, fruit fillings, ice cream, yogurt, dough, noodles, pasta, etc.) to impart desired viscosity, texture, mouthfeel, and consistency. Considering the commercial importance of starch-based systems in this research corn starch and wheat flour (consisting of ~75% starch) were considered as main research materials. This study was carried out focusing on both the ice phase and freeze concentrated matrix of the frozen system. During freezing, only the water molecules crystalize which is called ice phase; and some water remains unfrozen with the solute which is called freeze concentrated matrix. As for the ice phase, ice recrystallization kinetics and ice crystal size distribution were estimated. Simultaneously, for freeze concentrated matrix, the polymer distribution was observed using fluorescence microscope and molecular dynamics of water using dielectric relaxation technique has been carried out for the systematic understanding of ice recrystallization mechanism. Additionally, effect of antifreeze protein (AFP) on starch-based systems was considered in this research. AFPs are a class of polypeptides produced by certain cold-adapted species. It possesses a remarkable ability to adhere to the surface of ice crystals, significantly restricting their growth and inhibiting recrystallization. However, for maximizing the outcome knowledge on appropriate concentration and synergism with solute is required. The research was divided into four parts: (1) Ice recrystallization behavior of corn starch/sucrose solution, (2) Ice recrystallization behavior of wheat flour system, (3) Detailed analysis of the dynamic state of starch-sucrose solution by dielectric relaxation (4) Investigation of the effect of antifreeze protein III on ice crystal recrystallization behavior in corn starch and wheat flour system. The findings from each research part are shortly described below:

Part 1: Based on the principle of Ostwald ripening, ice recrystallization in corn starch (0.3 % and 3%, w/w)/sucrose (40 %, w/w) solution was examined at -10°C. The addition of corn starch to sucrose solution increased the rate constant of ice recrystallization. Fluorescence

microscopy was conducted to evaluate the distribution of corn starch molecules in order to figure out what was causing the increased ice recrystallization rate constant. According to the fluorescence micrograph, corn starch was found to distributed homogeneously in the freeze-concentrated phase. The analysis of ice crystal size distribution showed that at same average size the addition of corn starch increased the standard deviation. This finding indicated that the addition of corn starch widened the distribution of ice crystal size, which could be the mechanism causing increased ice recrystallization rate constant.

Part 2: The ice recrystallization kinetics of wheat flour system were examined under isothermal settings (-10 ℃) using the Ostwald ripening theory. The results showed that wheat flour (5 % w/w) robustly suppressed the ice recrystallization rate of sucrose solution (30 % w/w). To understand the ice recrystallization inhibition mechanism, the dynamics of unfrozen water in the freeze-concentrated phase of sucrose solution were investigated before and after addition of wheat flour. According to the dielectric relaxation analysis, wheat flour significantly increased the dielectric relaxation time (τ_2) and dielectric strength ($\Delta\varepsilon_2$). The result indicated that wheat flour can form strong interactions with water molecules, immobilizing them in the freeze-concentrated phase of sucrose solution. The results of this study suggest that wheat flour inhibits ice recrystallization by reducing the mobility of water in the freeze-concentrated matrix. The findings of this study may encourage the application of wheat flour as a cheap cryoprotectant in the frozen food industry.

Part 3: The molecular mobility of water in the freeze-concentrated matrix was explored in this section. Due to the non-equilibrium nature of the unfrozen serum phase, water molecules have a natural inclination to migrate from the water-polymer matrix to the ice crystal surface. Relaxation technique was used to detect this type of movement. In this experiment, several concentrations of corn starch (0.1%, 1%, and 10%) were added to 40% sucrose solution and frozen at -10°C under isothermal conditions. To gain a comprehensive understanding of the dynamic state of water in the freeze concentrated matrix, dielectric characteristics of sucrose/corn starch were first determined at 25°C in an unfrozen state, and then the results were compared to those obtained at -10°C. The experiment was conducted at frequencies ranging from 130 MHz to 20 GHz. To fit the experimental data, double Cole-Cole functions were necessary. Three appropriate process parameters, namely dielectric relaxation time (τ), relaxation strength ($\Delta\varepsilon$), and relaxation time distribution (β), were extrapolated to get insight into the relaxation process. The concentration of starch was found to be a factor in relaxation processes I and II above freezing. The polymer effect was confirmed by an increase in relaxation time and a decrease in relaxation time distribution as starch concentration was increased. When frozen, however, the higher starch contents didn't make much of a difference. Although relaxation duration increased at increasing concentrations, the consistent relaxation time distribution and decreasing relaxation strength revealed that the hydration of corn starch might be impaired by sucrose molecules.

Part 4: In this section, antifreeze protein type III (AFP III) was added to corn starch and wheat flour system to evaluate its ice recrystallization inhibitory behavior. The sucrose solution was used as control. In presence of corn starch, smaller concentration of AFP III was required to reduce the recrystallization rate significantly in contrast to sole sucrose solution. The outcomes revealed that corn starch enhanced the activity of AFP III. As for the wheat flour, wheat flour itself showed ice recrystallization inhibition potential. And further addition of AFP III, cooperatively suppressed ice recrystallization even in very low concentration (µg/mL). The addition of AFP III reduced ice crystal size and size distribution in both starch-based systems studied. This study suggested that corn starch enhanced the activity of AFP III and treating the wheat flour system with antifreeze protein type III had cooperative effects on IR rate inhibition.

We have concluded with the remarks that corn starch increased ice recrystallization by broadening the ice crystal size distribution. The corn starch molecules dispersed homogeneously in the freeze concentrated phase and mobility of water in the freeze concentrated matrix showed concentration dependence. In addition of AFP III, corn starch demonstrated synergistic efficiency. On the other hand, wheat flour demonstrated ice recrystallization inhibition potential by lowering the unfrozen water mobility.