Ice recrystallization behavior of starch-based system

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博士学位論文要約
Summary

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The aim of this study was systematic understanding of ice recrystallization in starch-based system. Starch is a complex food-grade biopolymer. It has been used either as an additive or as the main raw material in many frozen foods (soups, sauces, fruit fillings, ice cream, yogurt, dough, noodles, and pasta) to impart characteristic 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 distribution was observed using fluorescence microscopy 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. Antifreeze glycoproteins and polypeptides (AFPs) are present in a wide variety of creatures that can endure under freezing conditions, including fish, insects, fungi, and plants. It exhibits an extraordinary ability to attach to the surface of ice crystals, considerably preventing their development and recrystallization. To optimize the outcome, however, knowledge of the optimal concentration and synergism of the solute is essential. The study was divided into four sections:

Part 1: Using the Ostwald ripening concept, we evaluated ice recrystallization at -10°C in a corn starch (0.3 and 3%, w/w)/sucrose (40 percent, w/w) solution. Corn starch increased the rate constant of ice recrystallization when added to sucrose solution. To determine what was generating the increased ice recrystallization rate constant, fluorescence microscopy was used to assess the dispersion of corn starch molecules. Corn starch was shown to be distributed homogeneously in the freeze-concentrated phase using the fluorescence microscopy. The examination of the ice crystal size distribution revealed that the addition of corn starch increased the standard deviation for the same average size. This result revealed that the addition of corn starch extended the distribution of ice crystal size, which may have resulted in an increase in the ice recrystallization rate constant.

Part 2: Under isothermal conditions (-10 °C), the ice recrystallization kinetics of wheat flour system were investigated utilizing the Ostwald ripening theory. Wheat flour (5 % w/w) significantly reduced the ice recrystallization rate of sucrose solution (30 % w/w). To further understand the mechanism of ice recrystallization inhibition, we examined the dynamics of unfrozen water in the freeze-concentrated phase of sucrose solution before and after adding wheat flour. Wheat flour greatly enhanced the dielectric relaxation time (τ_2) and dielectric strength ($\Delta\varepsilon_2$). The results suggested that wheat flour can develop strong connections with water molecules, immobilizing them in sucrose solution's freeze-concentrated phase. According to the findings of this investigation, wheat flour prevents ice recrystallization by limiting the mobility of water in the freeze-concentrated matrix. The outcomes of this study may encourage the use of wheat flour in the frozen food industry as a low-cost cryoprotectant.

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 concluded by stating that corn starch promoted ice recrystallization by increasing the size distribution of the ice crystals. In the freeze concentrated phase, the corn starch molecules dispersed uniformly, and the mobility of water in the freeze concentrated matrix was concentration dependent. Along with AFP III, corn starch exhibited synergistic efficacy. Wheat flour, on the other hand, inhibited ice recrystallization by limiting the unfrozen water mobility.