

学 位 論 文 の 要 旨

論文題目 Glass transition and caking properties of amorphous carbohydrate blend
and maca (*Lepidium meyenii* Walpers) powders

(非晶質糖類混合およびマカ (*Lepidium meyenii* Walpers) 粉末のガラス転移と
固着特性)

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Maca (*Lepidium meyenii* Walp.) is a carbohydrate-rich vegetable root of the Brassicaceae family, native to the central Andes of Peru. Consumption of maca as functional food has been encouraged due to its bioactive compounds including glucosinolates, macaenes and macamides. The majority of maca roots are dehydrated and milled into a powder.

Commonly, food powders are at least partially amorphous, showing glass-to-rubber transition (glass transition) upon changes on temperature and water content. The glass transition of amorphous powder is characterized by the glass transition temperature (T_g). Amorphous powders are physically stable in the glassy state ($T < T_g$) because their macroscopic molecular mobility is very low. In contrast, amorphous powders are physically unstable in the rubbery state ($T > T_g$). The T_g of hydrophilic amorphous powders decreases with increasing water content because of the water plasticizing effect. Consequently, glass transition can also occur by a change of water content or water activity (a_w), even at constant temperatures.

Caking is a physical deterioration in which free-flowing powders are agglomerated into lumps, due to deformation and bridging of sticky particles as a result of plasticization and decrease of surface viscosity. Due to the fact that glassy powders are free-flowing, but rubbery powders are sticky and susceptible to agglomeration, the effect of water content on the T_g (T_g -curve) is useful to predict the caking of amorphous food powders.

Although maca is an outstanding food material, there has been little effort to understand its physical properties in comparison with its chemical and physiological properties. In particular, the glass transition and caking properties of maca powder have not been reported. Therefore, the purpose of this study was to understand the glass transition and caking properties of maca powders. In addition, amorphous carbohydrate blend powders were employed as food powder models, and predictive approaches for the caking of food powders were proposed.

In chapter 1, introduction and purpose of this thesis were shown as mentioned above. In chapter 2, fundamentals for the experiments were explained.

In Chapter 3, a commercially available maca powder was employed, and X-ray diffraction, starch gelatinization, water sorption, glass transition, and caking properties of the maca powder were investigated. From the X-ray diffraction pattern and enthalpy change for starch gelatinization, it was suggested that starch in the maca powder became largely amorphous during production of the maca powder. Effect of water content on the T_g of the maca powder was investigated using a differential scanning calorimetry (DSC). The maca powder showed a broad glass transition behavior reflecting a continuously distributed glass transition. From the T_g -curve, critical water content (w_c) was evaluated as the water content at $T_g = 25$ °C. Furthermore, the w_c was converted to critical water activity (a_{wc}) through the water sorption isotherm (equilibrium water content versus a_w). As expected, there was negligible caking in the glassy state ($a_w < a_{wc}$). In the rubbery state ($a_w > a_{wc}$), the degree of caking and hardness of cake of maca powder gradually increased with increase in a_w . Since maca powder showed a continuously distributed glass transition, the molecular mobility required for caking will have been provided incrementally by the increase in a_w above a_{wc} .

In Chapter 4, browning, starch gelatinization, water sorption, glass transition, and caking properties of the freeze-dried maca powders were investigated, and the results were compared with those for the commercial maca powder. The freeze-dried maca powders had lower browning and starch gelatinization than the commercial maca. There was a minor difference in

the anhydrous T_g (79.5~80.2 °C) and in a_{wc} among the samples. The degree of caking could be described uniformly as a function of a_w/a_{wc} , and the behavior was characterized by a stretching exponential function. This equation is mathematically equivalent to the Avrami equation. The Avrami model describes effect of annealing time on the degree of crystallization at a constant temperature. Given that crystallization is an orderly aggregation of molecules, the Avrami equation is analogically applicable for the caking (agglomeration) of powders. A novel modification of the proposed equation is that the Avrami equation was changed from “time-dependency” of crystallization to “ a_w -dependency” of caking.

In Chapter 5, freeze-dried water-soluble MD and plasticizers (glucose, maltose, and sorbitol) blend powders were employed as model food powders, and glass transition and caking behaviors were investigated. In order to characterize the difference in the dependence of viscosity on a_w in the rubbery state, the T_g -range (temperature-difference between onset and offset of glass transition) was evaluated from DSC thermograms. In addition, the T_g -range was corresponded to a_{wc} -range (a_w -difference between onset of and offset of a_{wc}). The T_g -range and a_{wc} -range increased by the addition of plasticizers because of the distributed molecular mobility in the rubbery state. In addition, it was confirmed that the distributed molecular mobility affected the degree of caking. The T_g -range was converted to the dependence of viscosity on a_w , and a predictive model for the caking of water-soluble amorphous powders was proposed based on the T_g -range.

In Chapter 6, the effect of cellulose content on the T_g -range, mechanical relaxation, and degree of caking of MD-glucose blend powder was investigated, and the degree of caking was analyzed by three approaches (a_w/a_{wc} , predicted η , and isothermal mechanical relaxation). Firstly, the degree of caking was described as a function of a_w/a_{wc} according to Chapter 4, and characterized by a stretched exponential function depending on the water-insoluble dispersion content. Secondly, the degree of caking was described as a function of log predicted η according to Chapter 5, and characterized by a linear function depending on the water-insoluble dispersion

content. Thirdly, the degree of caking was described as a function of degree of isothermal mechanical relaxation (ΔF), and characterized by a linear function independent of a_w and cellulose content. Among the three approaches, the characterization based on ΔF will have been a practical and useful approach to predict caking behavior, as ΔF can be rapidly evaluated. In addition, maca powders partially obeyed the linear function.

In Chapter 7, general conclusion and future subjects were explained. It was concluded that the characterization based on ΔF will be a practical and useful approach to predict caking behavior of amorphous food powders. This approach, however, is somewhat phenomenological, as the ΔF value will depend on the experimental conditions more or less (measurement time and initial compression). For the application of this approach to practical food powders, it is necessary to clarify the physical meaning of ΔF . In addition, the effect of powder composition on the relationship between the degree of caking and ΔF should be understood in more detail. Amorphous part of maca will have been constructed by protein, partially gelatinized starch, and sugar. In particular, protein is an electrically charged polymer, and thus its electrostatic repulsive effects will affect the caking behavior. For the better understanding of the caking behavior of amorphous food powders, these will be important subjects.