Glass transition and water sorption of spray dried mussel meat hydrolysate

Silva V.M. [1#], Park K.J.[2] and Hubinger M.D. [1*]
[1] Faculty of Food Engineering University of Campinas - Campinas, Brazil
[2] Faculty of Agriculture Eng. University of Campinas - Campinas, Brazil
vmsilva@fea.unicamp.br

INTRODUCTION

Mussels have a desirable and unique taste and aroma with application as flavorings in beverages, soups and sauces, however, their native protein do not directly contribute to flavor. In order to do so, they must first be broken down into smaller peptides or free amino acids that can then either impart taste or act as flavor precursors. These flavor-active breakdown products are generally formed by hydrolytic reactions or thermal breakdown. Hydrolysis can be achieved by treatment with enzymes, acids or alkalis however enzymatic hydrolysis is preferred due to its faster reaction rates, mild conditions, and high specificity (Tarté et al. 2006).

Protein hydrolysates are highly perishable due to their high moisture and protein content, for this reason, a process of microencapsulation by spray drying can be used to improve their shelf lives, trapping volatile flavor and producing a flavoring powder which can be incorporated into food formulations. The stickiness of the product during spray drying, caking and agglomeration of powders during processing and storage are some of the properties which are related to the glass transition temperature; the main cause of these phenomena is water sorption inducing the plasticization of the particle surface (Bhandari et al., 1999; Champion et al. 2000). As protein hydrolysates contain low molecular weight peptides, they have a low glass transition temperature, making necessary the use of carrier agents in order to increase the Tg value reducing stickiness and wall deposition in spray dryer.

The objective of this work was to collect experimental data of water sorption and glass transition temperatures of pure mussel hydrolysate powder and formulated ones with maltodextrin and gum Arabic, in order to obtain information about powders'stability.

MATERIAL AND METHODS

Material : The mussel hydrolysate was prepared using the protease Protamex®, at following experimental conditions: a water:meat ratio of 1:2, temperature of 51ºC, enzyme:substrate ratio of 4.5% w/w and pH of 6.85. The carrier agents used were: maltodextrin MOR-REX® 1910 (Corn Products, Mogi-Guaçu, Brazil) with 10 DE and gum Arabic (Colloides Naturels Brazil, São Paulo, Brazil). The main characteristics of the mussel protein hydrolysate obtained were 92.01 $\pm$ 0.02 of moisture, 5.83 $\pm$ 0.03 of proteins, 0.36 $\pm$ 0.03 of lipids and 0.89 $\pm$ 0.07 of ash.

Spray drying : Before the spray drying process, carrier materials were added directly in the concentration of 15% (w/w), selected in a preliminary study, to the protein hydrolysate with magnetic stirring, until complete dissolution, at room temperature. Spray drying process was performed in a laboratory scale spray dryer Labmaq MSD1 (Ribeirão Preto, Brazil), with a 1.2 mm diameter nozzle and main spray chamber of 500 mm x 150 mm. The mixture (at 25ºC) was fed into the main chamber through a peristaltic pump, the feed flow rate used was of 0.8 kg/h, drying air

flow rate was 36 m^3/h, compressor air pressure was 0.25 MPa and compressor air flow rate of 2.4 m^3/h. Inlet air temperature was 180°C and outlet air temperature varied of 100 ± 5ºC to for each experimental. The powders were characterized with 4.79, 11.75 and 11.78 µm of mean diameter particle, 2.97, 1.15 and 1.42% of moisture (w.b.) and 42.7, 18.6 and 23.9 g/100 g dry solids for hygroscopicity, for pure hydrolysate, with addition of 15 % of maltodextrin and 15% of gum Arabic, respectively.

Sorption isotherms : Sorption isotherms were determined by the gravimetric method. Eight saturated salt solutions were prepared (LiCl, CH_3COOK, $MgCl_2$, K_2CO_3, $Mg(NO_3)_2$, KI, NaCl and KCl) in order to provide relative humidity values of 11.3%, 22.6%, 32.8%, 43.2%, 52.9%, 68.9%, 75.3% and 84.3%, at 25°C temperature, respectively (Greenspan, 1977).

Glass transition temperature : The glass transition temperature was determined by differential scanning calorimeter, TA-MDSC-2920 (TA Instruments, New Castle, USA) equipped with a mechanical refrigeration system (RCS – refrigerated cooling accessory). Mussel hydrolysate powder samples of about 3 mg were placed into differential scanning calorimeter (DSC) aluminum pans (20 mL) and equilibrated over saturated salt solutions in desiccators at 25ºC, for 2 weeks. After equilibrium was reached, samples were hermetically sealed, weighed and taken for DSC analysis. Samples were heated at 10ºC/min from -70 to 120ºC and an empty pan was used as reference. Depending on the sample moisture contents, different initial and final temperatures were used. Two runs were performed for each sample, once the second scanning reduces the enthalpy relaxation of the amorphous powder, which appears in the first scan, thereby enhancing the accuracy of T_g measurement on the DSC thermogram. Equipment calibration was performed with indium ($T_{melting}$ = 156.6ºC) and verification with azobenzol ($T_{melting}$ = 68.0ºC). Dry helium, 25 mL/min, was used as the purge gas. All analyses were done in triplicate and data were treated by the software Universal Analysis 2.6 (TA Instruments, New Castle, USA).
The plasticizing effect of water on glass transition was described by the Gordon-Taylor model (Gordon et al., 1952).

RESULTS AND DISCUSSION

The values of equilibrium moisture content and the glass transition temperatures of mussel hydrolysate powders, pure and with the different carrier agents, stored at different water activities, are shown in Figure 1 and Table 1, respectively.

The results of water sorption showed an increase in equilibrium moisture content with increasing water activity, at the constant temperature of 25°C, with a good fit of the experimental data to modified BET model (R^2 > 0.994 and an average relative error less than 12.4%). Similar isotherms were observed for protein hydrolysates of fish and chicken breast (Aguilera et al., 1993; Kurozawa et al., 2009). According to Figure 1, the pure hydrolysate showed the highest water adsorption, followed by gum Arabic and maltodextrin 10 DE. Such differences can be explained by the composition of the carrier agents compared to pure hydrolysate; the pure hydrolysate contains peptides of low molecular weight, with low Tg, and then it is characterized by its high hygroscopicity (42.7 g/100g dry solids). Comparing the carrier agents, gum Arabic has a great number of ramifications with hydrophilic groups and therefore, can easily adsorb moisture from the ambient air than maltodextrin 10 DE that is less hydrolyzed, showing less hydrophilic groups and thus adsorbing less water. The visual appearance of the powders was observed, and pure hydrolysate adsorbed more water and as a result of this a liquefaction occurred at water activities

higher than 0.328, however powders formulated with both carrier agents present higher stability, with the appearance of a free flowing powder at water activities lower than 0.689.

A_w	Pure	15% MD	15% GA
0.11	8.1 ± 2.1	57.4 ± 1.5	54.4 ± 1.1
0.22	4.1 ± 1.0	56.8 ± 0.3	51.6 ± 2.7
0.32	3.8 ± 0.4	40.1 ± 1.6	45.8 ± 3.7
0.43	-6.1 ± 2.7	20.0 ± 1.6	25.7 ± 2.7
0.53	-13.6 ± 0.7	9.5 ± 0.6	7.2 ± 1.3
0.69	-44.3 ± 0.9	5.4 ± 0.9	5.3 ± 0.5
0.75	-60.3 ± 2.1	-6.8 ± 0.2	-10.7 ± 0.7
0.84	-62.1 ± 2.9	-39.3± 0.3	-39.8 ± 1.1

A_w: water activity; MD: maltodextrin; GA: gum Arabic

Table 1: Glass transition temperatures.

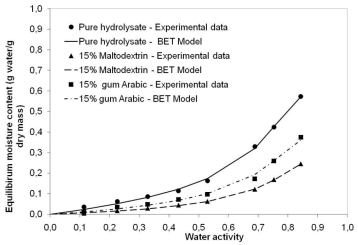

Figure 1: Water sorption isotherms.

The values of glass transition temperatures obtained for each powder stored at different water activities are shown in Table 1. The glass transition temperature was taken as the mid point of the glass transition (Roos, 1995). The glass transition temperatures of mussel protein hydrolysate are in good agreement with those reported for freeze-dried fish protein hydrolysate (Aguilera et al., 1993). The low T_g value of mussel protein hydrolysate was due to the presence of low molecular peptides resulted from enzymatic hydrolysis. Hashimoto et al. (2004) observed higher Tg values for freeze-dried whole fish muscles and Medina-Vivanco et al. (2007) also obtained higher Tg values for fresh tilapia fillets, certainly due to the presence of high molecular weight food polymers, myofibrillar proteins, such as myosin and actin.

The experimental data of T_g showed a good fit to the Gordon-Taylor model, showing and average relative error lower than 3%. The estimated parameters T_{gs}, k (Gordon Taylor model coefficient) and R^2 for pure hydrolysate were 24.9°C, 2.25, 0.979, for 15% of maltodextrin were 58.4°C, 3.76, 0.929 and for 15% of gum Arabic were 62.9°C, 2.71, 0.947, respectively.

In Table 1, the effect of carrier agents, maltodextrin or gum Arabic, on the glass transition temperature of mussel protein hydrolysate can be observed. The addition of carrier agents leads to an increase the Tg values. The same behavior was also observed for chicken meat hydrolysate, with addition carrier agents (Kurozawa et al., 2009). The authors obtained a T_{gs} of 44.43ºC for the pure chicken meat hydrolysate protein powder, while the addition of 10% of maltodextrin or gum Arabic led to Tgs values of 91.90 and 94.70, respectively. According to Table 1, the glass transition temperature decreased with increasing moisture content due to the plasticizing effect of water. At high water activities this shift became clearer due to the increase on samples moisture content, as can be observed in water sorption curves. The same trend was observed for several protein foodstuff such as fish muscle and its protein fractions, abalone and chicken meat hydrolysate (Hashimoto et al., 2004, Sablani et al., 2004, Kurozawa et al., 2008).

The critical conditions of storage, critical values of water activity (a_{wc}) and moisture content (X_c), for mussel protein hydrolysate were found by sorption isotherms and Tg data, at the temperature of 25ºC. The values found were a_{wc} = 0.02 and X_c = 0.01 g/g dry solids for pure hydrolysate, a_{wc} = 0.52 and X_c = 0.09 g/g dry solids for hydrolysate with 15% of maltodextrin, and a_{wc} = 0.54 and X_c = 0.10 g/g dry solids for hydrolysate with 15% of gum Arabic. This means that when the powder is stored at 25ºC, the maximum relative humidity to which it can be exposed is 2, 52 and 54% and its moisture content is of 1, 9 and 10%, for each formulation, respectively. The use of carrier agents resulted effectively in an increase in powder stability.

CONCLUSIONS

The experimental data were well fitted to modified BET model for sorption isotherms. Gordon-Taylor model was able to predict the strong plasticizing effect of water on Tg, with a great reduction in this value as water activity increases. The critical conditions for storage at 25ºC increased from 0.2 to 0.52-0.54 for critical water activity and critical moisture contents from 0.01 to 0.09 to 0.10 g/g dry solids, using carrier agents. Up to these values of relative humidity or at higher temperatures, at the same water activities, mussel powder hydrolysate can collapse and become sticky. The use of carrier agents increased powder stability.

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