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Effects of porous structure and water plasticization on the mechanical glass transition temperature and textural properties of freeze-dried trehalose solid and cookie

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ABSTRACT

This study aimed to examine the effects of porous structure and water plasticization on the mechanical glass transition temperature (T_g) of freeze-dried trehalose solid and cookie. The thermal T_g and mechanical T_g were evaluated by differential scanning calorimetry (DSC) and thermal rheological analysis (TRA), respectively. The mechanical T_g of the porous trehalose sample was slightly higher than that of the pellet sample. The mechanical T_gs for pellet and porous trehalose samples were higher than thermal T_g. Although pellet, crust, and crumb cookie samples showed indistinct glass transition behavior in the DSC thermograms, TRA revealed a clear glass transition. There were little differences in the mechanical T_g of the cookie samples. The mechanical T_g decreased with an increase in water content, and mechanically and thermally critical water contents (water content at $T_g = 25$ °C) were evaluated. Fracture properties of the cookie sample changed discontinuously at the thermally critical water content.

1. Introduction

Physical properties of dry foods can change drastically at their glass transition temperature (T_g). As a consequence, it is practically important to understand the impact of water content on the T_g of dry food systems. For example, the texture of bakery products changes from brittle to ductile because of water sorption (Payne and Labuza, 2005a). Such deterioration in properties can be explained by the glass transition concept: the T_g of a product decreases with increasing water content owing to the plasticizing effect of water, and thus, the glassy product turns into a rubbery product as a result of water sorption when its T_g decreases below room temperature (typically 25 °C).

Differential scanning calorimetry (DSC) has been widely used to evaluate T_g of amorphous materials. However, it is commonly difficult to detect T_g of food systems, because multiple thermal responses are continually observed, and thus glass transition is overlapped. In addition, since starch and starch-based foods show a small and broad endothermic shift, it is difficult to determine the T_g from the endothermic shift. In such cases, thermomechanical approaches to the determination of T_g such as thermal mechanical analysis (TMA), thermomechanical compression test (TMCT), and dynamic thermal mechanical analysis (DMTA) can be effective. For example, T_g of rice (Thuc et al., 2010), barley (van Donkelaar et al., 2015), spaghetti (Rahman et al., 2011) peas (Pelgrom et al., 2013), dairy powders (Hogan et al., 2010), abalone (Sablani et al., 2004), and chocolate wafers (Payne and Labuza, 2005b) has been determined using these mechanical approaches. In our previous study (Kawai et al., 2014), thermal rheological analysis (TRA), which is essentially equivalent to TMA and TMCT, was conducted and the effects of water content and sugar composition on the mechanical T_g of hand-made cookies were investigated. In the TRA measurement, the sample is compressed at a temperature below T_g, and heated up to a temperature above T_g. Then, T_g of the sample can be detected as a force drop induced by glass transition.

The thermal T_g observed by DSC has a clear physical meaning, representing a temperature at which the molecular relaxation time

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and viscosity are approximately 100 s and 10^{12} Pa·s, respectively (Angell et al., 1994). Mechanical T_g, on the other hand, depends strongly on experimental conditions and is thus often found to vary from the thermal T_g. This variation is most likely the reason why mechanical T_g is not always used as a critical factor in assessing the texture change of glassy foods (Nicholls et al., 1995; Le Meste et al., 1996). In addition, it has been suggested that the mechanical T_g can be affected by the sample structure. Currently, however, this point remains controversial. For example, Kasapis et al. (2007) investigated effect of porosity on the mechanical T_g of solid dried apple using small-deformation dynamic-oscillation measurements. They demonstrated that mechanical T_g decreased with increase in porosity. The authors concluded that the differences observed in the value of T_g with mechanical and thermal techniques were not an experimental artifact but a reflection of the distinct property and distance scale. On the other hand, Ross et al. (2002) investigated the effect of porosity on the mechanical T_g of synthetic and starch-based polymers using DMTA. The authors demonstrated that higher porosity is associated with lower mechanical T_g and concluded therefore that the effect of porosity on mechanical T_g was an artifact of DMTA.

To further investigate the roles of porous structure and water plasticization on the glass transition temperature and textural properties of amorphous samples, freeze-dried trehalose solid and a cookie product were employed, and the mechanical T_g of porous and pellet forms was investigated by TRA. The values of mechanical T_g were compared with the thermal T_g values observed by DSC. Since the cookie structure is comprised essentially of a highly dense outer layer (crust) and a porous interior (crumb), mechanical T_g was determined for three cookie samples, i.e., crust, crumb, and pellet. Finally, to confirm the practical importance of T_g, the effect of glass transition on cookie fracture properties was investigated.

2. Materials and methods

2.1. Sample preparations

Trehalose dihydrate (≥99%) was provided by Hayashibara Co. Ltd. Okayama, Japan. A 20% trehalose aqueous solution was dispensed into cylindrical holes (20 mm in diameter and 10 mm in depth) in a mold and frozen at −25 °C for 16 h. The frozen trehalose was placed on a pre-cooled stage (−35 °C) in a freeze-dryer and freeze-dried at <70 Pa with the temperature increasing from −35 °C to 5 °C over 35 h at a rate of approximately 1.7 °C/h. The freeze-dried solid was removed from the mold, yielding a porous glassy trehalose solid sample. A freeze-dried solid generally has numerous pores as a result of ice-sublimation. The mean porosity of the porous trehalose sample was expected to be approximately 0.8, because approximately 80% water was evaporated from the frozen trehalose solid. A fraction of the prepared porous glassy trehalose solid was ground with a mixer to give a glassy trehalose powder that was used in the preparation of the pellet sample (porosity = 0) and for DSC measurement.

A commercially available plain cookie (Bourbon Co. Nigata, Japan) was purchased in a local market. According to the product information, the protein, fat, and carbohydrate contents were 5.71%, 23.47%, and 67.76% (w/w), respectively. The mass, diameter, and thickness of the product (mean ± SD, n = 19) were 3.36 ± 0.20 g, 29.41 ± 0.85 mm, and 10.70 ± 0.46 mm, respectively.

2.2. Water content and water activity (a_w)

The samples were dried by vacuum drying at 105 °C (for cookie) and at 40 °C (for trehalose) for more than 12 h. The fully dried samples were equilibrated at 25 °C for 14–21 days in a desiccator with various types of saturated salts; LiCl (a_w = 0.11), CH_3COOK (a_w = 0.23), $MgCl_2$ (a_w = 0.33), K_2CO_3 (a_w = 0.43), $Mg(NO_3)_2$ (a_w = 0.53), NaBr (a_w = 0.58), and NaCl (a_w = 0.75). The water content (g-H_2O/100 g-DM) of all samples was examined gravimetrically by drying at 105 °C for 12 h. All tests were performed in triplicate and the results were averaged. A portion of all humid samples (a_w = 0.11–0.33) was also used for DSC and TRA measurements as described in subsequent section. To obtain values of anhydrous thermal and mechanical T_g, the dried samples were further vacuum-dried at 105 °C for 12 h prior to the DSC and TRA measurements.

2.3. DSC measurement

Thermal T_g was evaluated using a DSC (DSC 120; Seiko Instruments Inc. Tokyo, Japan). Temperature and heat flow were calibrated using indium and distilled water, and alumina powder was used as a reference material. The sample (20–30 mg) was placed into an aluminum DSC pan, and hermetically sealed. Heating scan was performed in the temperature range between 0 and 150 °C at a heating rate of 5 °C/min. T_g was determined from an onset point of the endothermic shift due to glass transition using software interfaced with the DSC. All tests were performed in triplicate, and the results were averaged.

2.4. TRA measurement

TRA measurement was carried out according to the procedure described in our previous study (Kawai et al., 2014) with minor modifications. Schematic drawings of the TRA procedure for the porous sample (a) and pellet sample (b) are shown in Fig. 1. Briefly, a heating stage was attached to a texture analyzer (CR-150; Sun Scientific Co. Ltd. Tokyo, Japan). The heating stage was controlled using a temperature controller (TNX-400E; As One Co. Osaka, Japan) with a K-type thermocouple located at the surface of the sample stage. Temperature change at the surface of the sample stage was independently measured by a data logger (TC-08; Pico Technology Ltd. Cambridgeshire, UK) with another K-type thermocouple. The temperature was confirmed using iced water (0 °C) and melting temperature of stearic acid given by DSC measurement (69.0 °C).

For the analysis of pellet samples, powder material (20–30 mg) was placed in a stainless die (diameter = 3 mm), and the sample was pushed down to the bottom. The die including the pellet sample (height = 2.7–4.5 mm) was put on the heating stage of the texture analyzer, and the sample was compressed with a plunger (3 mm in diameter) directly at 20 or 80 N (2.83 or 11.3 MPa). The compression was held for 1 min, and then the sample was heat-scanned at a rate of 3 °C/min in the temperature range between 10 and 125 °C.

Porous samples (approximate diameter × height = 20 mm × 10 mm for trehalose, 29 mm × 11 mm for cookie crust, and 22 mm × 8 mm for cookie crumb) were covered with a wrap film (Asahi Kasei Co. Tokyo, Japan) to prevent water evaporation during the measurement. The trehalose sample was used without further treatment. The cookie sample, on the other hand, is comprised mainly of a crust (high density part) and crumb (porous part). For the TRA measurement of the cookie crust, the entire cookie was used directly since the crust covers the crumb. By contrast, the cookie crust was removed carefully with a knife to expose the crumb structure for the TRA analysis of the crumb. The samples were placed on the sample stage and compressed at a constant force (20 N for trehalose and 30 N for cookie) with a plate plunger (diameter = 30 mm). The force applied to each sample was slightly lower than its fractural force, which