

(1) Article Type: Regular paper

(2) Running Title: Effect of trehalose content on the texture of deep-fried wheat flour particles

(3) Full Title: Effects of trehalose content and water activity on the fracture properties of deep-fried wheat flour particles and freeze-dried porous waxy corn starch solids

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(6) List of Abbreviations

$a_w$ , water activity;  $a_{wc}$ , critical water activity; DM, dry matter;  $\Delta F$ , the force difference between initial compression and compression after 3 min;  $T_g$ , glass transition temperature.

(7) Any Necessary Footnotes: Not applicable

## Abstract

Wheat flour-based batter containing 0% to 20% trehalose was deep-fried, dried and held in various water activity ( $a_w$ ) conditions. The effects of trehalose content and  $a_w$  on oil content, water sorption, isothermal mechanical relaxation, and fracture properties were investigated. For comparison, the fracture properties of freeze-dried porous waxy corn starch solids were also investigated. The 10% trehalose sample had the lowest oil content, water content, and  $a_w$ . A force-reduction value ( $\Delta F$ ) of the samples was evaluated as a typical mechanical relaxation parameter.  $\Delta F$  gradually increased with increasing  $a_w$  and sharply increased above a specific  $a_w$  presumed to be associated with the glass to rubber transition. Compared to  $\Delta F$  values among the glassy samples, 10% and 20% trehalose samples had higher  $\Delta F$  values (were more rigid) than 0% and 5% trehalose samples. From the fracture measurements of the glassy samples, the first fracture force increased linearly and the number of fracture peaks decreased linearly with increasing  $a_w$ . At each  $a_w$ , 10% trehalose had the lowest first fracture force and the highest the number of fracture peaks. Freeze-dried porous waxy corn starch solids showed similar fracture properties to deep-fried samples. These findings suggest that around 10% trehalose content is optimal for producing deep-fried foods with a brittle texture.

Key words: Trehalose, Glass to rubber transition, Water activity, Fracture property, Texture, Deep-frying

## INTRODUCTION

Dry food products are commonly supplied in an amorphous state, and as such, they are in a glassy state below the glass transition temperature ( $T_g$ ) and in a rubbery state above.<sup>1)2)</sup> A glass to rubber transition also occurs due to water sorption, even at a constant temperature, because the  $T_g$  of hydrophilic amorphous materials decreases with an increase in water content or water activity ( $a_w$ ). When the  $T_g$  of glassy food products decreases below room temperature (typically 25 °C) by water sorption, the food products become rubbery. Glassy food products are characterized as having a brittle texture that changes to a ductile texture due to a glass to rubber transition.<sup>3)4)5)</sup> Thus, the effect of water content or  $a_w$  on  $T_g$  is an important factor in controlling the texture of dry food products.<sup>6)7)8)</sup>

Deep-fried foods are one type of dry food products. In the case of “tempura”, various physical changes, such as starch gelatinization, dehydration, and oil uptake occur as competing or synergistic effects in the batter phase during the deep-fry process,<sup>9)10)11)12)</sup> to produce the fry coating that covers food products. After cooking, tempura is allowed to cool at room temperature, and the fry coating is thought to become glassy, at least on the outer part, producing a fry coating with a favorable brittle texture. When the hold time at room temperature is prolonged, the fry coating changes to a ductile texture because glass to rubber transition occurs through water sorption originating from the atmosphere and/or from the coated food products. Practically, it is important to maintain the favorable brittle texture of the fry coating for as long as possible.

In our previous study,<sup>5)</sup> the effects of corn starch and trehalose on glass to rubber transition and texture properties were investigated in a deep-fried food model (deep-fried wheat flour particles). From these results, the 10% trehalose-added sample had a higher

$T_g$  and more brittle fracture properties than samples with no added trehalose or with the addition of corn starch. Although trehalose has been suggested to be an effective texture modifier for deep-fried foods, the optimal content to produce a maximally brittle texture has not been clarified. The purpose of this study, thus, was to understand the effect of trehalose content on the fracture properties of deep-fried wheat flour particles as a function of  $a_w$ . For comparison, fracture properties of freeze-dried porous waxy corn starch solids were also investigated. Waxy corn starch is a simple component (amylopectin) in comparison to wheat flour (mixture of amylopectin, amylose, and wheat protein). In addition, freeze-drying is non-thermal processing, and thus chemical reactions and thermal degradation will be greatly limited.

## **MATERIALS AND METHODS**

### ***Materials***

Wheat flour containing 8% protein and less than 1.7% lipid as reported in product information (Nisshin Flour Milling Inc., Nagoya, Japan), trehalose dihydrate (Hayashibara Co., Ltd., Okayama, Japan), and waxy corn starch (Sigma-Aldrich Co., St. Louis, MO, USA), and canola oil (J-Oil Mills, Inc., Tokyo, Japan) were used.

### ***Preparation of deep-fried wheat flour particles***

Deep-fried wheat flour particles were prepared as reported previously with minor modifications.<sup>5)</sup> A sufficient amount of the canola oil was placed in the chamber of a digital oil bath (EOS-200RD; AS ONE Co., Osaka, Japan), and the temperature was set to 180 °C with agitation at 250 rpm by a magnetic stir bar (diameter, 8 mm and length, 30 mm). Batter was prepared by mixing wheat flour and chilled water at a weight

ratio of 1.0 : 1.6. For trehalose-added samples, 5%, 10%, and 20% trehalose (anhydrous trehalose weight per dry wheat flour weight) was added into the mixture, which was held in an ice water bath. Batter (approximately 4 ml) was dropped by pipette over a period of 30 to 40 s into the oil from a hole (5 mm). The batter was deep-fried at 180 °C for 4 min. The deep-fried samples were scattered on a stainless-steel tray with mesh (7 mm × 7 mm), and allowed to cool at room temperature for approximately 4 min. Then, the samples were put into a bag until analysis.

### ***Oil content of deep-fried samples***

Oil content of the deep-fried samples was evaluated by the Soxhlet extraction method.<sup>13)</sup> The samples were manually ground, and vacuum dried at 110 °C (stage temperature) for 8 h. The fully dried samples (1 g) were extracted with diethyl ether at 60 °C for 12 h. All samples were prepared and assayed in triplicate, and the results were averaged.

### ***Water sorption isotherm***

Deep-fried samples were vacuum dried at 110 °C (stage temperature) for 8 h. The fully dried samples were equilibrated at 25 °C for at least 2 weeks in a desiccator with various saturated salt solutions: LiCl ( $a_w = 0.113$ ), CH<sub>3</sub>COOK ( $a_w = 0.225$ ), MgCl<sub>2</sub> ( $a_w = 0.328$ ), K<sub>2</sub>CO<sub>3</sub> ( $a_w = 0.432$ ), Mg(NO<sub>3</sub>)<sub>2</sub> ( $a_w = 0.529$ ), NaBr ( $a_w = 0.576$ ), KI ( $a_w = 0.689$ ), and NaCl ( $a_w = 0.755$ ). Equilibrium water content (g/100 g-dry matter, DM) of the samples was determined gravimetrically by vacuum drying at 110 °C (stage temperature) for 8 h. For comparison, water content of the deep-fried samples for which  $a_w$  was not adjusted

(unadjusted) was also determined. All measurements were performed in triplicate and the results were averaged.

The water sorption isotherm was analyzed by fitting experimental data to the Guggenheim-Anderson-de Boer (GAB) model (Eq. 1),

$$W = \frac{W_m \cdot C \cdot K \cdot a_w}{(1 - K \cdot a_w) \cdot (1 + (C - 1) \cdot K \cdot a_w)} \quad (\text{Eq. 1})$$

where  $W$  and  $W_m$  are the equilibrium water content (g/100 g-DM) and the monolayer water content (g/100 g-DM), respectively.  $C$  and  $K$  are correction factors for the sorption properties of the first layer with respect to the bulk liquid and for the properties of the multilayer with respect to the bulk liquid, respectively.<sup>14)</sup> Fitting analysis was carried out using KaleidaGraph software (version 3.6, Hulus Inc., Tokyo, Japan).

#### ***Isothermal mechanical relaxation***

Isothermal mechanical relaxation behavior of the deep-fried samples was investigated using a texture analyzer (CR-150; Sun Scientific Corp., Ltd., Tokyo, Japan) as described previously.<sup>4)5)</sup> The samples (14-16 particles) were set into the sample cup holder (diameter, 31.90 mm and height, 9.95 mm) and then placed on the stage (25 °C) of the texture meter. The samples were compressed at 80 N with a plate plunger (diameter, 30 mm) and held in the compressed condition for 3 min. From the force-time curve, the force-drop ( $\Delta F$ ) between the initial force and the force after 3 min was evaluated as the degree of isothermal mechanical relaxation for a given condition.<sup>4)5)</sup> The measurements were performed in triplicate and the results were averaged.

#### ***Sample preparation of freeze-dried porous waxy corn starch solid***

Freeze-dried waxy corn starch solids were prepared by the method of Sogabe et al. with

modification.<sup>3)</sup> Waxy starch (5 g, dry basis) was placed in a vial, and distilled water was added to produce 90% water content. For the trehalose-added samples, 5%, 10%, and 20% trehalose (as anhydrous trehalose weight per dry waxy corn starch weight) was added. A magnetic stir bar was placed into each vial, and the vials were covered by wrapping with film. The vials were placed in a boiling water bath (approximately 98 °C) and heated for 10 min with magnetic stirring to prevent the sedimentation of starch granules at the initial stage of the heating. The samples were then cooled to room temperature and put into cylindrical holes (diameter, 20 mm and height, 10 mm) in a mold and frozen at -25 °C for 16 h. The frozen samples were placed on a pre-cooled stage (-35 °C) in a freeze-dryer and freeze-dried at approximately 11 Pa with an increase in temperature from -35 °C to 5 °C over 34 h. The freeze-dried solids with numerous pores formed by ice sublimation were removed from the mold and vacuum-dried at 110 °C (stage temperature) for 8 h. The fully dried samples were equilibrated at 25 °C for at least two weeks in a desiccator under  $a_w = 0.113$ , 0.225, and 0.328 as described above.

### ***Texture properties***

The fracture properties of the deep-fried and freeze-dried samples were evaluated at 25 °C using a texture meter (CR-500DX; Sun Scientific Corp., Ltd., Tokyo, Japan). Each deep-fried sample was put on the sample stage and then compressed with a plate plunger (diameter, 30 mm) at 0.5 mm/s. Each freeze-dried sample was put on the sample stage and then compressed with a plunger (diameter, 5 mm) at 0.5 mm/s. In the force-deformation curve, the fracture force was evaluated from the first fracture point. In addition, the total number of fracture peaks was counted in the deformation range of 2.5

mm.<sup>4)5)</sup> For each deep-fried and freeze-dried sample, measurements were performed five times, and the results were averaged.

### ***Statistical analysis***

Analysis of variance (ANOVA) with Turkey's HSD test ( $p < 0.05$ ) was performed using KaleidaGraph software (version 3.6, Hulinks Inc.)

## **RESULTS AND DISCUSSION**

### ***Oil content of deep-fried samples***

The effect of trehalose content on oil content for deep-fried samples (unadjusted  $a_w$ ) is shown in Table 1. Oil content of 0% and 10% trehalose samples obtained in this study was in good agreement with values obtained in our previous study (53% for no added trehalose sample and 42% for 10% trehalose sample).<sup>5)</sup> The oil content significantly decreased and then increased slightly with an increase in trehalose content. Trehalose is a water-soluble disaccharide and thus prevents oil uptake in deep-fried foods. Tavera-Quiroz et al. (2012)<sup>15)</sup> reported that water-soluble materials (methylcellulose-glycerol-sorbitol mixtures) reduce oil uptake during the frying process. Similar behavior was observed in corn-gum, wheat gum mixtures,<sup>16)</sup> wheat-cellulose derivatives, and wheat-sorbitol mixtures.<sup>17)</sup> Lee and Inglett<sup>18)</sup> demonstrated that oat bran, which has a high water holding capacity, contributed to the reduction of oil content of deep-fried samples.

Among samples, the 10% trehalose sample had the lowest oil content. A major component of wheat flour is amylopectin. Since amylopectin is a large polymer having many branched segments, oil uptake is facilitated by the many gap spaces of the segments in the dehydrated state. Trehalose is thought to be located in the internal and interfacial



parts of amylopectin. Since internal trehalose can fill the gap spaces of amylopectin, oil uptake is reduced. In the case of 20 % trehalose sample, it is thought that the amount of interfacial trehalose increased essentially and generated further gap spaces among the trehalose molecules; oil-uptake was promoted slightly. The internal and interfacial trehalose concept is discussed along with other experimental results below.

### ***Water sorption isotherm of deep-fried samples***

Water sorption isotherms (equilibrium water content versus  $a_w$ ) at 25 °C for deep-fried samples are shown in Fig. 1. The samples show a sigmoidal pattern for water sorption, similar to that for other amorphous starchy foods.<sup>19)20)</sup> The water sorption isotherms were obtained by fitting experimental data to the GAB model (Eq. 1), and GAB parameters ( $W_m$ ,  $C$ , and  $K$ ) are summarized in Table 1. The  $W_m$  values (2.48-2.71 g/100 g-DM) were in good agreement with values for no added trehalose (2.69 g/100 g-DM) and 10% added trehalose samples (2.44 g/100 g-DM) reported in our previous study.<sup>5)</sup> The  $C$  and  $K$  values, on the other hand, were slightly higher and lower, respectively, than those of the previous study. It should be noted that the GAB parameters are sensitive to differences in experimental values, and even a small difference in experimental values may result in amplified differences in GAB parameters.<sup>21)22)</sup> As well known, chemical, physical, and biological properties of food are controlled not by water content, but by  $a_w$ .<sup>23)24)</sup> Thus, GAB parameters were used to transform water content determined experimentally to  $a_w$ .

The effect of the trehalose content on the water content of deep-fried samples (unadjusted  $a_w$ ) is shown in Table 1. The water content of 10% and 20% trehalose samples was significantly lower than that of 0% and 5% trehalose samples. From the water sorption isotherm with GAB parameters (Fig. 1),  $a_w$  of the samples was estimated (Table

1). Similar to the trend for water content, 10% and 20% trehalose samples had significantly lower  $a_w$  than 0% and 5% trehalose samples, indicating that a higher trehalose content in the batter promoted water evaporation during deep-frying. During deep-frying of batter, wheat starch gelatinizes at around 60 °C,<sup>25)26)</sup> and water evaporation subsequently occurs at around 100 °C. When wheat starch gelatinizes in the presence of trehalose, the trehalose is partially incorporated into the gelatinized wheat starch due to hydrophobic interaction induced by oil, and the trehalose acts as internal trehalose, as suggested earlier. Since water molecules are excluded from gelatinized wheat starch by internal trehalose molecules, evaporation of water is promoted by the addition of trehalose.

#### ***Isothermal mechanical relaxation behavior of deep-fried samples***

Representative isothermal mechanical relaxation measurements at 25 °C are shown in Fig. 2. The force of the samples decreased with increasing hold time due to mechanical relaxation. Mechanical relaxation nearly reached equilibrium during the measurement. The 0% trehalose sample with  $a_w = 0.113$  showed very little mechanical relaxation, suggesting that it is in a glassy state (high elasticity). In contrast, the 0% trehalose sample with  $a_w = 0.529$  showed high mechanical relaxation, suggesting that it is in a rubbery state (low elasticity). The 10% trehalose samples had much lower mechanical relaxation than the 0% trehalose samples at each  $a_w$ . As a typical parameter,  $\Delta F$  (the force difference between initial compression and compression after 3 min) was evaluated from the isothermal mechanical relaxation curves as described in previous studies.<sup>5)27)28)</sup>

The effect of  $a_w$  on  $\Delta F$  of deep-fried samples is shown in Fig. 3. The  $\Delta F$  increased linearly with increasing  $a_w$ , but became much greater above a characteristic  $a_w$  that depended on trehalose content. The glass to rubber transition occurs at the  $a_w$  due to water

plasticizing. Commonly, the  $a_w$  for which the glass to rubber transition occurs at 25 °C has been described as the critical water activity ( $a_{wc}$ ).<sup>29)</sup> The  $a_{wc}$  of 0% and 10% trehalose samples is reported to be 0.509 and 0.649, respectively.<sup>5)</sup> It should be noted that the  $a_{wc}$  values are within the turning range of the  $a_w$ -dependency of  $\Delta F$ .

In a comparison of the  $\Delta F$  values for glassy samples (open symbols in Fig. 3), 10% and 20% trehalose samples had much lower  $\Delta F$  values than 0% and 5% trehalose samples, suggesting that these samples were of a more rigid, glassy material than 0% and 5% trehalose samples. Taking the suggestion that internal trehalose fills the gap spaces in amylopectin, molecular structure of the amylopectin is thought to be physically strengthened. This is also the reason why 10% and 20% trehalose samples can maintain their glassy state up to a higher  $a_w$  than 0% and 5% trehalose samples can.

After deep-frying, the deep-fried samples are in a non-steady state with a graduated water content and temperature distribution between the inner and outer parts, depending on hold time. Although the relationship between location in the sample and hold time impacts the physical state of samples in ways that were not understood in this study, 0% and 5% trehalose samples were roughly in the rubbery state, while 10% and 20% trehalose samples were in the glassy state, based on the  $a_w$  of samples (unadjusted  $a_w$ ). The addition of 10% and 20% trehalose is expected to improve the brittle texture of the fry coating. For a better understanding, the effect of  $a_w$  on the fracture properties is discussed below.

### ***Fracture properties of deep-fried and freeze-dried samples***

For quantitative interpretation, the first fracture force (arrow) and the number of fracture peaks were evaluated from the force-distance curves. Typical force-deformation curves for 0% and 10% trehalose samples with  $a_w = 0.113$  and  $a_w = 0.529$  are shown in

Fig. 4. The 10% trehalose sample with  $a_w = 0.113$  showed numerous and small fracture peaks, suggesting a brittle texture (Fig. 4-a).<sup>5)</sup> This is supported by the suggestion that the sample was in the glassy state under this condition (Fig. 3). The 0% trehalose sample with  $a_w = 0.113$ , on the other hand, showed a larger peak with a smaller number of fractures than the 10% trehalose sample. The 10% trehalose sample showed a larger peak and smaller number of fractures for  $a_w$  increased to 0.529 (Fig. 4-b); the sample is expected to be in a glassy state (Fig. 3). The 0% trehalose sample, on the other hand, showed a much larger fracture peak, suggesting ductile texture<sup>5)</sup>; in fact, the sample was suggested to be in a rubbery state (Fig. 3).

The effect of  $a_w$  on the first fracture force of the deep-fried samples is shown in Fig. 5-a for samples expected to be in both the glassy (open symbols) and rubbery (closed symbols) states based on data shown in Fig. 3. The first fracture force increased linearly with increasing  $a_w$  in the glassy state. At each  $a_w$  in the range for which all the samples are in the glassy state (0.113-0.432), the 10% trehalose sample showed a significantly lower value than the others, except at  $a_w = 0.225$  and 0.432 for the 10% versus 20% trehalose samples. There were no significant differences between 0% and 5% trehalose samples. At the rubbery state near the glassy state, the first fracture force showed a maximum value because of large deformation for the ductile fracture. At higher  $a_w$ , the first fracture force markedly decreased with an increase in  $a_w$  as a result of softening in the rubbery state. There were no clear differences in values among the rubbery samples with various trehalose contents.

The effect of  $a_w$  on the number of fracture peaks for deep-fried samples in the glassy (open symbols) and rubbery (closed symbols) states based on data shown in Fig. 3 is shown in Fig. 5-b. The number of fracture peaks decreased linearly with increasing  $a_w$  in

the glassy state. At each  $a_w$  in the range for which all the samples are in the glassy state (0.113-0.432), the 10% and 20% trehalose samples had significantly higher values than the 0% and 5% samples (except at  $a_w = 0.225$  for 5%, 10%, and 20% trehalose samples). There was no significant difference between 10% and 20% trehalose samples. In the rubbery state, the differences among samples with various trehalose levels were negligible.

For comparison, fracture properties of freeze-dried porous waxy corn starch solids with varying trehalose levels were investigated in the low  $a_w$  range between 0.113 and 0.328. The effect of  $a_w$  on the first fracture force of the freeze-dried samples is shown in Fig. 6-a. The first fracture peak increased with increasing  $a_w$ . At each  $a_w$ , the 0% trehalose sample had a significantly higher value than the others. The 10% trehalose sample, on the other hand, had a significantly lower value than the others (except for 10% versus 20% trehalose at  $a_w = 0.113$ ). There was no significant difference between 5% and 20% trehalose samples. The effect of  $a_w$  on the number of fracture peaks of the freeze-dried samples is shown in Fig. 6-b. The number of fracture peaks decreased with an increase in  $a_w$ . At each  $a_w$ , the 10% trehalose sample had a significantly larger value than the others (except for 0% versus 10% trehalose at  $a_w = 0.113$ ). There were no significant differences among the 0%, 5%, and 20% trehalose samples (except for 0% and 20% versus 5% at  $a_w = 0.225$ ), and these showed an almost equivalent behavior to those of deep-fried samples.

### ***General discussion of fracture properties***

From the fracture studies, deep-fried samples containing 10% trehalose were shown to have the lowest first fracture force and the highest number of fracture peaks, suggesting that the 10% trehalose sample had a more brittle texture than the others. A similar effect

of 10% trehalose addition was also confirmed in freeze-dried samples. It is essentially impossible to compare the fracture properties between deep-fried wheat flour particles and freeze-dried waxy corn starch solids, because they are largely different gluten, amylose, and fat contents and thermal history. However, the fact that there were similar effects of trehalose on the fracture properties between deep-fried wheat flour particles and freeze-dried waxy corn starch solids suggests that molecular interaction between trehalose and amylopectin is a major factor for the texture modification. These are discussed using model drawings (Fig. 7) as follows.

As discussed above, internal and interfacial trehalose molecules are thought to mainly exist in amylopectin (Fig. 7-a). Internal trehalose fills the gap spaces in amylopectin, and amylopectin is thus physically strengthened. Interfacial trehalose, on the other hand, separates amylopectin molecules with intermolecular hydrogen bonding. Intermolecular interactions between interfacial trehalose and amylopectin, however, largely do not develop due to steric hindrance. Since fractures basically occur at the physically weak points in the structure, the interactions between interfacial trehalose and amylopectin act as fracture points. Thus, the first fracture force was decreased and the number of fracture peaks was increased by the addition of trehalose. When excess trehalose is added in the system, the amount of interfacial trehalose increases, and the interaction between interfacial trehalose and amylopectin causes physical strengthening. These results suggest that addition of around 10% trehalose is an optimum level to improve the brittle texture of fry coating.

Water is thought to intrinsically act similar to trehalose in amylopectin. However, the first fracture force increased linearly and the number of fracture peaks decreased linearly with increasing  $a_w$ , even in the glassy state. In addition,  $\Delta F$  decreased with the addition

of trehalose but increased linearly with increasing  $a_w$ . These contrary effects of water on trehalose can be explained by differences in the dynamics of amylopectin. As is well-known, water has a much lower molecular size and much higher molecular mobility than trehalose. Water molecules within the glassy polymer are mobile at ambient temperature<sup>30)31)</sup> and small enough to pass through the polymeric network. Thus, in the case of water, there will be an unclear distinction between internal and interfacial molecules in glassy amylopectin. Water molecules can fill gap spaces in the internal and interfacial part of amylopectin that trehalose cannot sufficiently fill (Fig. 7-b). Since fracture points attributed to interactions between interfacial trehalose and amylopectin can be physically strengthened by water, the first fracture force increased linearly and the number of fracture peaks decreased linearly with increasing  $a_w$ , even in the glassy state. In addition, amylopectin has branched segments with varying chain lengths, and water will enhance the flexibility of the chains from short chain segments to long chain segments with increasing  $a_w$  as a local plasticizer. Thus,  $\Delta F$  increases with increasing  $a_w$  under the glassy state. When all chains become flexible by increasing  $a_w$ , a glass to rubber transition occurs, and the dependence of  $a_w$  on  $\Delta F$  becomes more apparent. Trehalose, on the other hand, is immobile in the glassy matrix because the large molecules cannot pass through the polymeric network unless the polymer matrix becomes mostly flexible (i.e., rubbery state).

## CONCLUSION

The effect of trehalose content on the fracture properties of deep-fried samples was investigated as a function of  $a_w$ . The first fracture peak decreased and the number of fracture peaks increased with increasing trehalose content. In addition, around 10%

trehalose was an optimum concentration to improve brittle texture. On the other hand, the first fracture peak increased and the number of fracture peaks decreased with increasing  $a_w$ . These results were discussed in the context of structure (internal and interfacial molecules) and dynamics (mobile and immobile molecules) in amylopectin. These results suggest that other types of sugar and sugar alcohols may also be effective for improving the brittle texture of fry coating. Although deep-fried wheat flour particles were employed as the fry coating model in this study, fry coating actually coats the food products, and water migration from the food stuff to the fry coating occurs quickly. In addition, deep-fried food products are in non-steady state, and thus there is a gradation (distribution) of water content and temperature between inner and outer parts depending on the hold time. Thus, it is important to understand the kinetic fracture properties of fry coating. These subjects will be taken up in further studies.

### **Conflicts of interest**

Kiyoshi Kawai (corresponding author) received a donation from Hayashibara Co., Ltd. (Okayama, Japan) for a study not reported here. The sponsor had no control over the interpretation, writing, and publication of this work.

### **Acknowledgments**

Financial support for this study was provided by JSPS KAKENHI (Grant-in-Aid for Scientific Research C: 18K05516).

### **References**

- 1) K. Kawai, I. Uneyama, S. Ratanasumawong, Y. Hagura, and K. Fukami: Effect of



- calcium maltobionate on the glass transition temperature of model and hand-made hard candies. *J. Appl. Glycosci.*, **66**(3), 89-96 (2019).
- 2) M.T. Kalichevsky and J.M.V. Blanshard: A study of the effect of water on the glass transition of 1: 1 mixtures of amylopectin, casein and gluten using DSC and DMTA. *Carbohydr. Polym.*, **19**(4), 271-278 (1992).
  - 3) T. Sogabe, K. Kawai, R. Kobayashi, J.S. Jothi, and Y. Hagura: Effects of porous structure and water plasticization on the mechanical glass transition temperature and textural properties of freeze-dried trehalose solid and cookie. *J. Food Eng.*, **217**, 101-107 (2018).
  - 4) J.S. Jothi, T. Ebara, Y. Hagura, and K. Kawai: Effect of water sorption on the glass transition temperature and texture of deep-fried models. *J. Food Eng.*, **237**, 1-8, (2018).
  - 5) J.S. Jothi, T.N.D. Le, and K. Kawai: Effects of trehalose and corn starch on the mechanical glass transition temperature and texture properties of deep-fried food with varying water and oil contents. *J. Food Eng.*, **267**, 109731 (2020).
  - 6) Y.H. Roos: Thermal analysis, state transitions and food quality. *J. Therm. Anal. Calorim.*, **71**(1), 197-203 (2003).
  - 7) S. Kasapis: Definition and applications of the network glass transition temperature. *Food Hydrocoll.*, **20**(2-3), 218-228 (2006).
  - 8) J. Blahovec: Role of water content in food and product texture. *Int. Agrophys.*, **21**(3), 209-215 (2007).
  - 9) R.P. Singh and N. Mermelstein: Heat and mass transfer in foods during deep-fat frying: Engineering aspects of deep-fat frying of foods. *Food Tech. (Chicago)*, **49**(4), 134-137 (1995).

- 10) P.Y. Thanatuksorn, C.P. Pradistsuwana, and P. Jantawat: Oil Absorption and Drying in the Deep Fat Frying Process of Wheat Flour-Water Mixture, from Batter to Dough. *Japan J. Food Eng.*, **6**(2), 143-148 (2005).
- 11) K. Bordin, M.T. Kunitake, K.K. Aracava, and C.S.F. Trindade: Changes in food caused by deep fat frying-A review. *Arch. Latinoam. Nutr.*, **63**(1), 5-13 (2013).
- 12) E.K. Oke, M.A. Idowu, O.P. Sobukola, S.A.O. Adeyeye, and A.O. Akinsola: Frying of food: a critical review. *J. Culin. Sci. Tech.*, **16**(2), 107-127 (2018).
- 13) AOAC: Official Methods of Analysis. 17th Edition, the Association of Official Analytical Chemists, Gaithersburg, MD, USA. Methods 925.10, 65.17, 974.24, 992.16 (2000).
- 14) M.S. Rahman: Water activity and food preservation. In *Handbook Food Preservation*, **20**, 448-471 (2007).
- 15) M.J. Tavera-Quiroz, M. Urriza, A. Pinotti, and N. Bertola: Plasticized methylcellulose coating for reducing oil uptake in potato chips. *J. Sci. Food Agri*, **92**(7), 1346-1353 (2012).
- 16) S. Sahin, G. Sumnu, and B. Altunakar: Effects of batters containing different gum types on the quality of deep-fat fried chicken nuggets. *J. Sci. Food Agri*, **85**(14), 2375-2379 (2005).
- 17) M.A. Garcia, C. Ferrero, N. Bertola, M. Martino, and N. Zaritzky: Edible coatings from cellulose derivatives to reduce oil uptake in fried products. *Innov. Food Sci. Emerg. Technol.*, **3**(4), 391-397 (2002).
- 18) S. Lee and G.E. Inglett: Effect of an oat  $\beta$ -glucan-rich hydrocolloid (C-trim30) on the rheology and oil uptake of frying batters. *J. Food Sci.*, **72**(4), 222-226 (2007).
- 19) A.H. Al-Muhtaseb, W.A.M. McMinn, and T.R.A. Magee: Moisture sorption

- isotherm characteristics of food products: a review. *Food Bioprod. Process.*, **80**(2), 118-128 (2002).
- 20) M.L. Kawas and R.G. Moreira: Characterization of product quality attributes of tortilla chips during the frying process. *J. Food Eng.*, **47**(2), 97-107 (2001).
- 21) M.S. Rahman and R.H. Al-Belushi: Dynamic isopiestic method (DIM): Measuring moisture sorption isotherm of freeze-dried garlic powder and other potential uses of DIM. *Int. J. Food Prop.*, **9**(3), 421-437 (2006).
- 22) S. Fongin, K. Kawai, N. Harnkarnsujarit, and Y. Hagura: Effects of water and maltodextrin on the glass transition temperature of freeze-dried mango pulp and an empirical model to predict plasticizing effect of water on dried fruits. *J. Food Eng.*, **210**, 91-97, 2017.
- 23) T. P. Labuza: The properties of water in relationship to water binding in foods: a review. *J. Food Process. Preserv.*, **1**, 167-190, 1997.
- 24) M. S. Rahman: Food stability beyond water activity and glass transition: macro-micro region concept in the state diagram. *Int. J. Food Prop.*, **12**, 726-740, 2009.
- 25) S.M. Yusop, M.Y. Maskat, and W.A. Mustapha: Effects of frying temperature, pressure, and time on gelatinisation of sago flour as compared to wheat and rice flour in fried coating. *Int. J. Food Sci. Technol.*, **46**(12), 2669-2675 (2011).
- 26) I. Contardo, J. Parada, A. Leiva, and P. Bouchon: The effect of vacuum frying on starch gelatinization and its in vitro digestibility in starch–gluten matrices. *Food Chem.*, **197**, 353-358 (2016).
- 27) A.E. Alvino Granados, S. Fongin, Y. Hagura, and K. Kawai: Continuously distributed glass transition of maca (*Lepidium Meyenii Walpers*) powder and impact on caking properties. *Food Biophys.*, **14**(4), 437-445 (2019).

- 28) K. Kawai, K. Sato, K. Lee, and S. Koseki: Effects of glass transition and hydration on the biological stability of dry yeast. *J. Food Sci.*, 86(4), 1343-1353 (2021).
- 29) Y.H. Roos: Time-dependent phenomena. in Phase Transitions in Foods. *Academic Press.*, San Diego, 193-245 (1995).
- 30) G. Roudaut, D. Simatos, D. Champion, E. Contreras-Lopez, and M.L. Mest: Molecular mobility around the glass transition temperature: a mini review. *Innov. Food Sci. Emerg. Technol.*, 5(2), 127-134 (2004).
- 31) K. Watanabe, K. Kawai, A. Nagoe, T. Suzuki, and M. Oguni: Multiple glass-transitions of globular protein BSA aqueous solutions depending on the hydration degree. *Bull. Chem. Soc. Jpn.*, 92, 729-737 (2019).

## Figure Legends

Fig. 1. Water sorption isotherms of the deep-fried samples with varying trehalose content.

Values are expressed as mean  $\pm$  SD (n = 3).

Fig. 2. Representative isothermal mechanical relaxation curves for deep-fried samples.

Fig. 3. Effect of  $a_w$  on the  $\Delta F$  of the deep-fried samples with varying trehalose content.

Values are expressed as mean  $\pm$  SD (n = 3). Open and closed symbols indicate that the samples are in the glassy state and rubbery state, respectively.

Fig. 4. Typical force-distance curves for deep-fried samples at (a)  $a_w = 0.113$  and (b)  $a_w = 0.529$ .

Fig. 5. Effect of  $a_w$  on (a) first fracture force and (b) number of fracture peaks for deep-fried samples with varying trehalose content. Values are expressed as mean  $\pm$  SD (n = 5).

Open and closed symbols indicate that samples are in the glassy state and rubbery state, respectively.

Fig. 6. Effect of  $a_w$  on (a) first fracture force and (b) the number of fracture peaks of freeze-dried waxy starch samples with varying trehalose content. Values are expressed as mean  $\pm$  SD (n = 5).

Fig. 7. Model drawings of (a) trehalose-added sample with low  $a_w$  under glassy state and (b) trehalose-added samples with high  $a_w$  under glassy state.

Table 1. Oil content, water content,  $a_w$ , and GAB parameters of the deep-fried samples

trehalose %	oil content g/100 g-DM	water content g/100 g-DM	$a_w$	$W_m$ g/100 g-DM	$C$	$K$	$R^2$
0	54.1±0.5 <sup>a</sup>	5.76±0.33 <sup>a</sup>	0.59±0.03 <sup>a</sup>	2.71	10.8	0.95	0.99
5	52.9±0.5 <sup>b</sup>	5.54±0.58 <sup>a</sup>	0.57±0.05 <sup>a</sup>	2.71	12.5	0.94	0.99
10	44.6±0.7 <sup>c</sup>	3.17±0.40 <sup>b</sup>	0.28±0.07 <sup>b</sup>	2.48	41.0	1.00	0.99
20	47.8±0.6 <sup>d</sup>	3.41±0.38 <sup>b</sup>	0.32±0.06 <sup>b</sup>	2.57	24.4	0.95	0.99

The values are expressed as mean ± SD ( $n = 3$ ).

Different letters indicates significant difference ( $p < 0.05$ ).

GAB parameters ( $W_m$ ,  $C$ , and  $K$ ) are fitting values.

The values of  $a_w$  are estimated from the water content by GAB parameters.

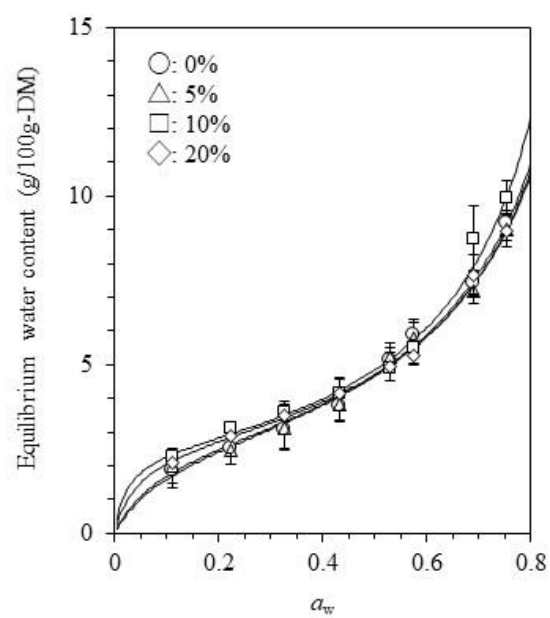


Fig. 1

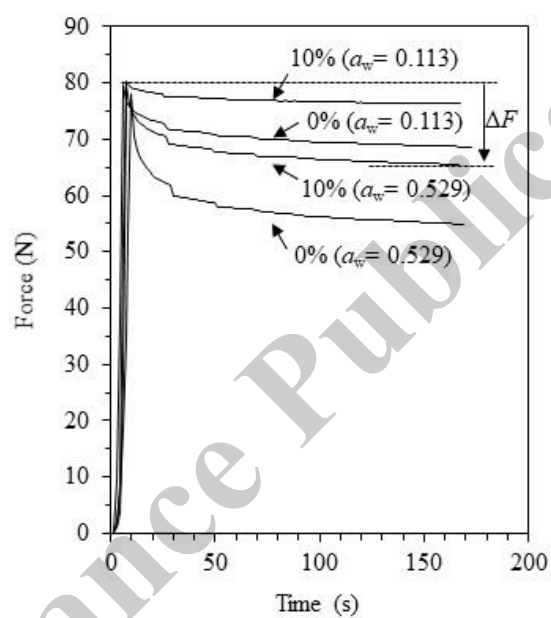


Fig. 2



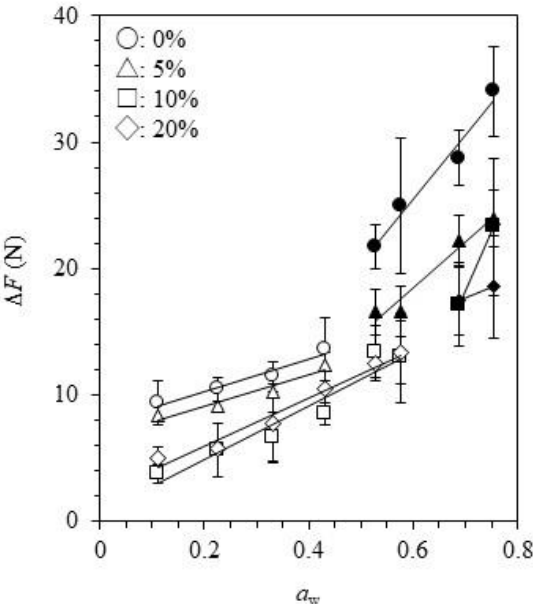


Fig. 3

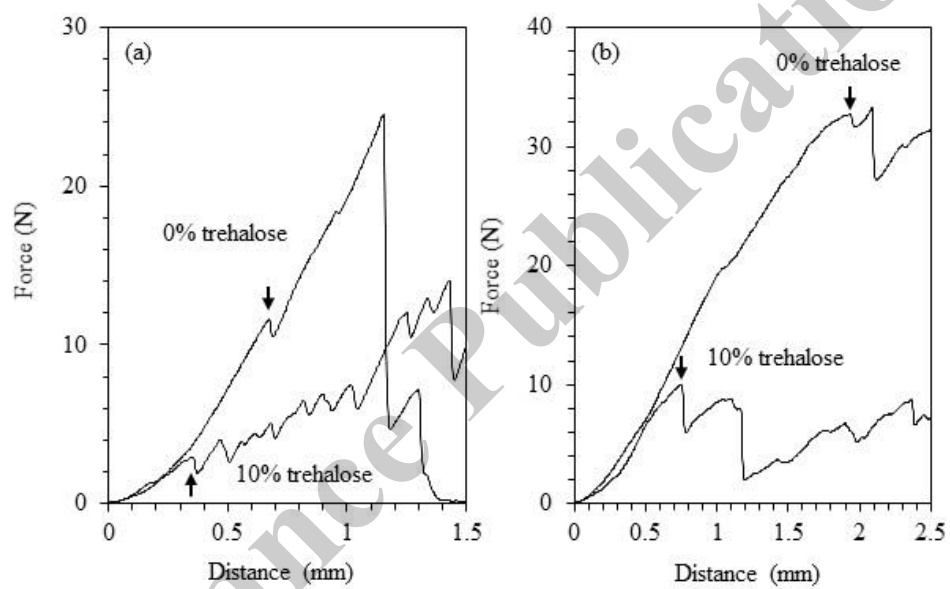


Fig. 4

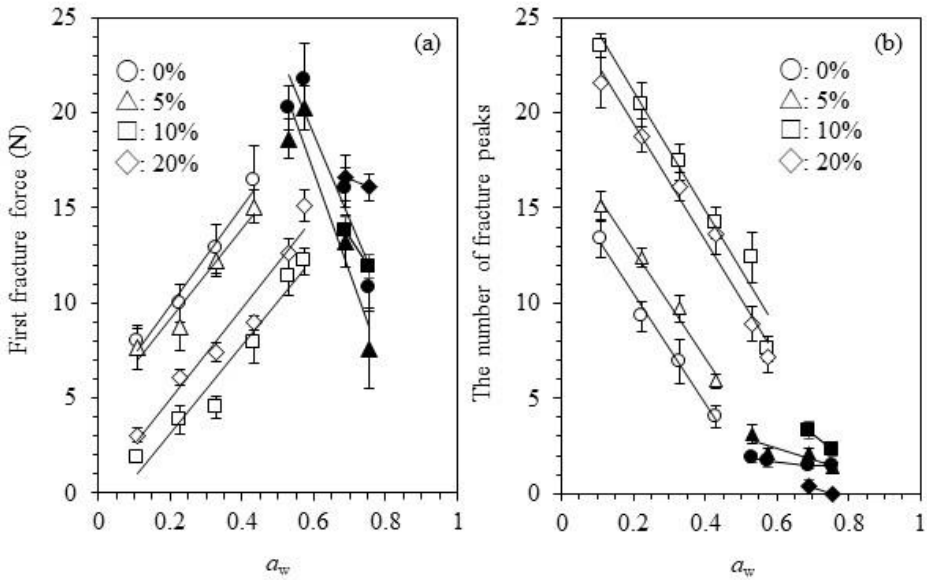


Fig. 5

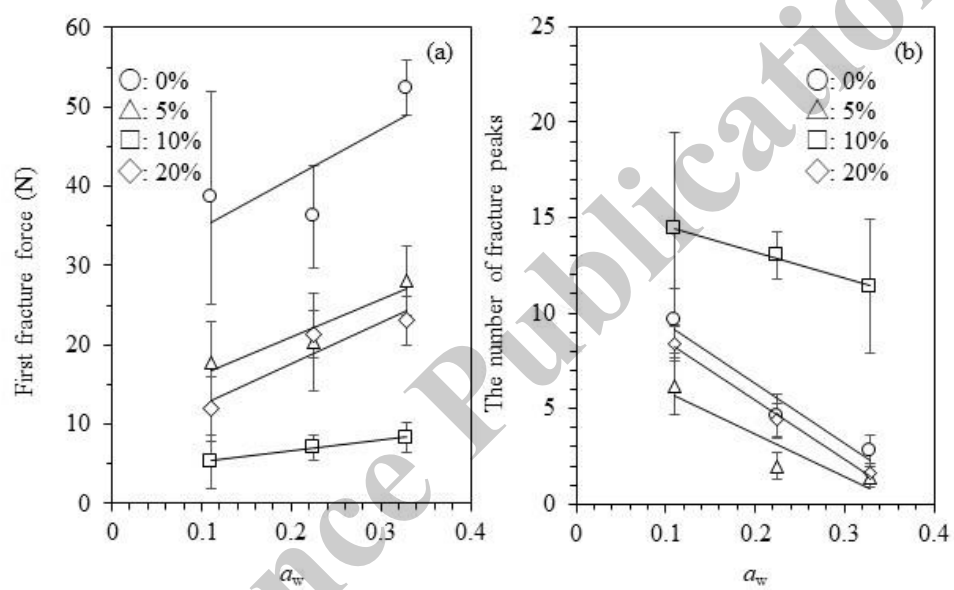
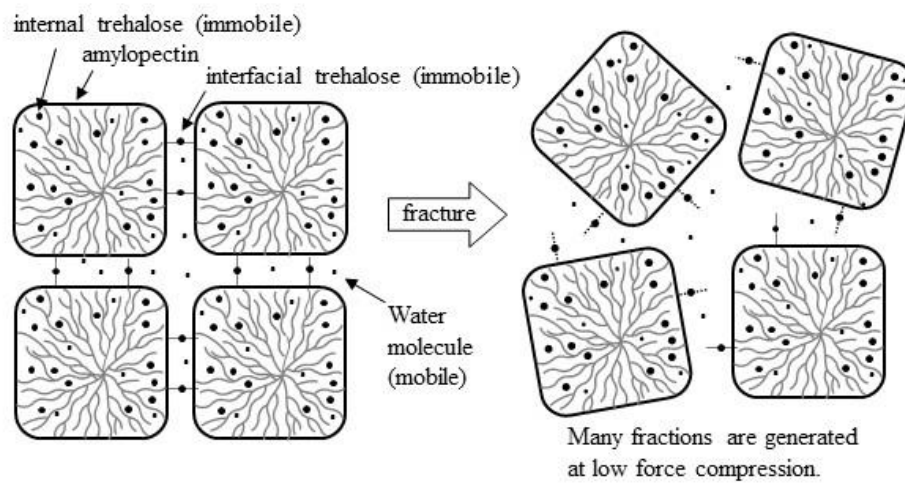


Fig. 6

(a) trehalose-added sample having a low  $a_w$  (glassy state)



(b) trehalose-added sample having a high  $a_w$  condition (glassy state)

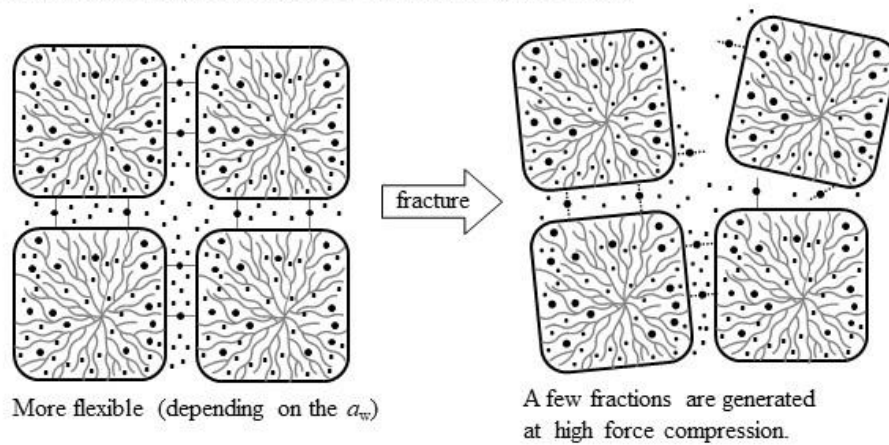


Fig. 7