

Thermal and dynamic mechanical properties of frozen wheat flour dough added with selected food gums

Sim, S. Y., Noor Aziah, A. A., Teng, T. T. and *Cheng, L. H.

School of Industrial Technology, Universiti Sains Malaysia, 11800 Minden, Penang, Malaysia

Abstract: The effects of food gums addition on wheat dough freeze-thaw and frozen storage stability were studied. Thermal and dynamic mechanical properties of frozen wheat dough without yeast addition were determined by means of Differential Scanning Calorimetry (DSC) and Dynamic Mechanical Analysis (DMA). DSC results revealed that food gums showed the ability to increase freeze-thaw stability in frozen-stored samples wherein lower difference in melting enthalpy between first and second freeze-thaw cycle was shown. Based on DMA results, in general, difference between T_g' and storage temperature (-18°C) of dough became smaller upon addition of food gums. This may have a practical implication whereby the unfrozen phase could be better protected against physical degradation.

Keywords: Dough, food gums, DSC, DMA

Introduction

There is a growing demand for frozen dough over the last two decades. Frozen dough can be manufactured in a centralized factory and distributed to retail outlets. This makes fresh bread available throughout the day and quality of the product can be controlled easily. This directly helps to reduce the production costs of bakery products (Asghar *et al.*, 2005; Yi and Kerr, 2009). However, prolonged storage of frozen dough has always resulted in dough with variable performance and longer proofing time, low loaf volume and poor texture of bread. This could be attributed to the degradation of dough molecules upon frozen storage (Kenny *et al.*, 1999; Asghar *et al.*, 2005).

Frozen wheat dough consists of an ice phase as well as an unfrozen phase with a very low freezing point. The low freezing point is attributed to freeze concentration of solutes in the unfrozen phase when water is removed as ice crystals during the freezing process. Within this unfrozen phase, deteriorations are taking place even at very low temperatures (Ribotta and Le Bail, 2007).

As freeze concentration progresses, yeast viability decreases progressively. The resultant low loaf volume can be overcome with a longer proofing time (Asghar *et al.*, 2005). Besides reduce in yeast viability, deterioration of frozen dough quality could be due to degradation in physical state of the frozen dough during storage (Laaksonen and Roos, 2001). Gluten network of a frozen dough could be weakened as a result of ice crystallization and recrystallization. This has given rise to longer proofing time and lower loaf volume of dough upon extended frozen storage

(Asghar *et al.*, 2005).

Lo and Ramsden (2000) stated that food gums commonly serves as additives to control the shelf-life stability and texture of frozen food products. Food gums when incorporated into frozen foods are able to minimize the negative effects of freeze-thaw cycles as it has high water holding capacity and helps to control water migration and also dough rheology (Kobs, 1997; Mandala *et al.*, 2007). Immobilization of water would lessen the formation of ice crystals and consequently prevent gluten network deterioration, decrease in frozen dough strength as well as injure of yeast cells (Sharadanant and Khan, 2003).

Several research works have been carried out on this issue. Sharadanant and Khan (2003) studied on ice crystallization and recrystallization of frozen dough upon incorporation of hydrophilic gums namely carboxymethylcellulose, locust bean gum, arabic gum and kappa-carrageenan. Ribotta and Le Bail (2007) investigated the effects of α -amylase, ascorbic acid, protease, hemicellulase, gluten and guar gum on the thermo-mechanical properties of dough at sub-zero temperature. Lo and Ramsden (2000) carried out research on the influence of locust bean gum and xanthan gum on freeze-thaw stability in starch gels and frozen dough.

Understanding the phase and state transitions taking place in doughs during freezing and frozen storage and the effects of other food ingredients on dough properties is essential in order to produce premium quality wheat dough (Laaksonen and Roos, 2001). Many researchers believed that when a dough system is stored below its T_g of the maximally freeze-concentrated unfrozen phase (T_g'), it is expected to be more stable; however, when it is stored above

*Corresponding author.

Email: hcheng@usm.my

Tel.: 60-4-6535209; Fax: 60-4-6573678

its T_g' , the difference between T_g' and the storage temperature will affect the rate of chemical, biological and physical reactions (Ribotta and Le Bail, 2007). Present study was done to determine the effects of different food gums addition on controlling ice crystallization and recrystallization in frozen wheat dough upon freeze-thaw cycles and frozen storage, and also the possibility to reduce the difference between sub-zero glass transition temperature of the dough and the practical frozen storage temperature.

Materials and Methods

Materials

Wheat flour with 10% protein (14% moisture basis), 0.47% ash, and 13.3% moisture contents in dry basis was obtained from United Malayan Flour Mill (Butterworth, Malaysia). Alginic acid Sodium salt from brown algae (Fluka brand, product of United Kingdom), Carboxymethylcellulose Sodium salt (Fluka brand, product of Switzerland), Psyllium husk (*Plantago ovata*) with 99.29% purity (Country Farms Sdn. Bhd., Selangor, Malaysia), Locust bean gum from *Cerantonia siliqua* seeds (Sigma-Aldrich brand, product of Morocco) and Konjac glucomannan (Hung Thong Food Technology Sdn. Bhd., Penang, Malaysia) were used in this study.

Sample preparation

Wheat flour was dry-blended with sodium alginate (ALG), carboxymethylcellulose (CMC), psyllium husk powder (PSY), locust bean gum (LBG) and konjac glucomannan (KGM) at addition levels of 0.2 and 0.8% w/w flour basis. These addition levels were arbitrarily fixed for screening purposes to cover both the highest and lowest limits use of the gums. Wheat flour without addition of food gums was served as control. The flour mixture was sifted with sieve of 30 mesh using high efficient noiseless separator (Model GY-450SSA, Kimah, Malaysia).

Dough samples used in this study was prepared using a Brabender Farinograph®-E (Brabender OHG, Duisburg, Germany). An amount of 300 g of wheat flour mixture with or without addition of food gums (corrected to 14% moisture basis) with addition of 62.5% distilled water was mixed in a 300-g mixing bowl for 9.5 min. The amount of water used and the dough mixing time were pre-determined with Brabender Farinograph up to an optimum consistency, i.e. 500 Brabender Units. These values were applied to all sample types in this study.

Differential Scanning Calorimetry (DSC)

Dough prepared was made into sheet with

constant thickness using a noodle machine. With the aid of a cork borer, a disc of the sample was prepared and placed in a hermetically sealed aluminium pan for freezer storage at -18°C for two months. The sample weight was approximately 10.0 ± 0.3 mg.

Analysis was done by means of a DSC-6 (Perkin-Elmer, USA) which was calibrated with mercury, distilled water and indium. The system was flushed with dry nitrogen gas at a flow rate of 20 mL/min to avoid any water vapour condensation in the heating chamber. Reference was consisted of an empty hermetically sealed aluminium pan. Below are the heating profiles:

- Step 1: Cool from 30°C to -60°C at $10^{\circ}\text{C}/\text{min}$
- Step 2: Hold at -60°C for 30 min
- Step 3: Heat from -60°C to 100°C at $10^{\circ}\text{C}/\text{min}$
- Step 4: Hold at 100°C for 2 min
- Step 5: Cool from 100°C to -60°C at $10^{\circ}\text{C}/\text{min}$
- Step 6: Hold at -60°C for 30 min
- Step 7: Heat from -60°C to 100°C at $10^{\circ}\text{C}/\text{min}$

Onset temperature (T_o), peak temperature (T_p), enthalpy (ΔH), and midpoint glass transition temperature ($T_{g, \text{midpoint}}^{**}$) were recorded. Triplicate measurements were performed for each dough samples.

Dynamic Mechanical Analysis (DMA)

A Dynamic Mechanical Analyzer (DMA 8000, Perkin Elmer) was used to perform the analysis. Dough was made into a slab of 10 mm length, 10 mm width and 2.75 mm thickness with a mould. The dough was stored in a freezer at -18°C overnight (>12 hours). During analysis, each dough sample was clamped with a Single Cantilever Bending geometry. Analysis was carried out with a heating rate of $2^{\circ}\text{C}/\text{min}$ from -100°C to 20°C . The data was collected at frequency scan of 1 Hz.

Storage modulus (G'), loss modulus (G'') and loss tangent ($\tan \delta$) were obtained from the thermogram. The phase and state transition temperatures were determined from the peak maximum in loss modulus (Ribotta and Le Bail, 2007). Each measurement was done in triplicate.

Statistical analysis

Where necessary, differences between treatment means were determined using Duncan test ($P < 0.05$) by SPSS software for Windows Release 15.0 (SPSS Inc., Chicago, Illinois, USA).

Results and Discussion

Differential Scanning Calorimetry (DSC)

Deterioration of dough during frozen storage and freeze-thaw cycles is believed to be associated to ice crystallization and recrystallization and is provoked with increasing number of freeze-thaw cycles (Varriano-Marston *et al.*, 1980; Inoue *et al.*, 1994; Naito *et al.*, 2004). Thawing and refreezing lead to loss of smaller size ice crystals during warming and growth of larger size ice crystals during refreezing (Zaritzky, 2008). Weakening of gluten network occurred due to the fact that the specific volume of ice is greater than that of liquid water (Nesvadba, 2008). As a result, the growth of large ice crystals within the gas pores of dough causes them to expand and disrupt the gluten-starch structure (Esselink *et al.*, 2003; Baier-Schenk *et al.*, 2005). Additionally, there is water distribution in dough matrix during frozen storage due to the presence of temperature gradients and thus water vapor pressure profile is created (Berglund *et al.*, 1991; Zaritzky, 2008). Growth of ice crystals also induces separation of the water molecules from the hydrophilic components of dough matrix (Luyet, 1968; Varriano-Marston, Hsu *et al.*, 1980). Thus, moisture loss may occur upon thawing and cause decrease in saleable weight besides deteriorating of dough quality (Nesvadba, 2008; Phimolsiripol *et al.*, 2008).

During freezing, ice crystals formation causes separation of dough matrix into frozen and unfrozen phase (Bot, 2003; Tananuwong and Reid, 2004; Ribotta and Le Bail, 2007). When the temperature was reduced to below sub-zero, the unfrozen phase becomes maximally concentrated as more and more water molecules crystallize into ice, ultimately this phase will remain unfrozen due to the high concentration of solutes present (Roos, 1992; Tananuwong and Reid, 2004). According to Akyurt *et al.* (2002), this unfrozen phase is highly viscous and hence showing low diffusion properties.

Freezing endotherm

Freeze-thaw stability of frozen dough

In this study, freeze-thaw stability of plain wheat flour dough with or without addition of food gums (i.e. sodium alginate, ALG; carboxymethyl cellulose, CMC; psyllium husk powder, PSY; locust bean gums, LBG; konjac glucomannan, KGM) at 0.2% and 0.8% flour basis addition levels were studied by means of DSC. Both fresh and 2-month frozen stored samples were subjected to two freeze-thaw cycles and the respective ice freezing and melting endotherms were

recorded. Tables 1 - 3 show the onset temperature (T_o), peak temperature (T_p), and enthalpy (ΔH) of dough samples obtained from both the ice freezing and melting endotherms.

Table 1. Onset temperature, T_o of freezing endotherm and melting endotherm of wheat flour dough with or without food gums added

| T_o (°C) of freezing endotherm | | | | |
|----------------------------------|-----------|-----------|-----------|-----------|
| Sample | Fresh | | 2 months | |
| | 1st Cycle | 2nd Cycle | 1st Cycle | 2nd Cycle |
| 0.2 % Addition level | | | | |
| Control | -13.54a | -22.88b | -14.08a | -23.06bc |
| ALG | -13.23a | -19.08a | -12.60a | -19.82a |
| CMC | -11.86a | -23.15b | -13.49a | -22.01b |
| PSY | -14.41a | -22.85b | -14.41a | -24.02c |
| LBG | -11.98a | -23.32b | -11.22a | -23.70c |
| KGM | -11.66a | -23.08b | -11.81a | -23.32bc |
| 0.8 % Addition level | | | | |
| Control | -13.54A | -22.88B | -14.08A | -23.06B |
| ALG | -13.03A | -17.66A | -13.31A | -17.64A |
| CMC | -14.27A | -22.43B | -13.89A | -22.14B |
| PSY | -12.35A | -22.00B | -14.91A | -21.64B |
| LBG | -12.75A | -24.35B | -13.64A | -20.88B |
| KGM | -11.53A | -23.04B | -12.73A | -23.78B |
| T_o (°C) of melting endotherm | | | | |
| Sample | Fresh | | 2 months | |
| | 1st Cycle | 2nd Cycle | 1st Cycle | 2nd Cycle |
| 0.2 % Addition level | | | | |
| Control | -1.45ab | -3.91ab | -1.94a | -4.61b |
| ALG | -1.84b | -4.37b | -1.73a | -4.14a |
| CMC | -1.49ab | -3.86ab | -1.78a | -4.16a |
| PSY | -1.74ab | -4.29b | -1.72a | -4.13a |
| LBG | -1.19a | -3.45a | -1.79a | -4.25a |
| KGM | -1.45ab | -3.88ab | -1.66a | -4.08a |
| 0.8 % Addition level | | | | |
| Control | -1.45A | -3.91AB | -1.94A | -4.61B |
| ALG | -1.37A | -3.52A | -2.01A | -4.23AB |
| CMC | -1.77A | -4.21B | -1.51A | -3.94A |
| PSY | -1.43A | -3.68AB | -1.83A | -4.06AB |
| LBG | -1.83A | -4.21B | -1.75A | -4.10AB |
| KGM | -1.88A | -4.15AB | -1.75A | -4.15AB |

ALG=sodium alginate; CMC=carboxymethyl cellulose; PSY=psyllium husk powder; LBG=locust bean gum; KGM=konjac glucomannan
Means (n = 3) within a column with the same letter are not significantly different at the 5% probability level.

Freezing endotherm T_o values (Table 1) of control samples decreased from -13.54 to -22.88°C and -14.08 to -23.06°C, for the fresh and frozen stored samples, respectively. Similar trend was evident for freezing endotherm T_p values. The T_p values after first and second freeze-thaw cycle decreased from -13.82 to -23.60°C for the fresh control sample while from -14.13 to -23.91°C for frozen stored control sample (Table 2). As for the freezing endotherm ΔH values (Table 3), which served as an indicator of amount of freezable water present in dough, were found to decrease from 84.51 to 62.76 J/g and 87.59 to 59.58 J/g for fresh and frozen stored control samples, respectively, after first and second freeze-thaw cycle. The decrease in freezing endotherm T_o , T_p and ΔH values upon dough freeze-thaw cycles is expected and it could be attributable to the increasing release of solutes from the metastable dough matrix into the maximally freeze-concentrated unfrozen phase.

Table 2. Peak temperature, T_p of freezing endotherm and melting endotherm of wheat flour dough with or without food gums added

| T_p (°C) of freezing endotherm | | | | |
|----------------------------------|-----------|-----------|-----------|-----------|
| Sample | Fresh | | 2 months | |
| | 1st Cycle | 2nd Cycle | 1st Cycle | 2nd Cycle |
| 0.2 % Addition level | | | | |
| Control | -13.82a | -23.60b | -14.13a | -23.91c |
| ALG | -13.40a | -20.22a | -12.89a | -20.60a |
| CMC | -12.36a | -23.60b | -13.58a | -22.44b |
| PSY | -14.49a | -23.55b | -14.43a | -24.53c |
| LBG | -12.51a | -23.89b | -11.55a | -24.38c |
| KGM | -11.95a | -23.74b | -11.98a | -23.84c |
| 0.8 % Addition level | | | | |
| Control | -13.82A | -23.60B | -14.13A | -23.91B |
| ALG | -13.50A | -18.83A | -13.57A | -19.50A |
| CMC | -14.49A | -23.24B | -14.11A | -23.21B |
| PSY | -12.70A | -22.68B | -14.98A | -22.29B |
| LBG | -12.97A | -24.87B | -13.68A | -21.68AB |
| KGM | -11.75A | -23.61B | -12.88A | -24.26B |
| T_p (°C) of melting endotherm | | | | |
| Sample | Fresh | | 2 months | |
| | 1st Cycle | 2nd Cycle | 1st Cycle | 2nd Cycle |
| 0.2 % Addition level | | | | |
| Control | 3.67ab | 2.24ab | 2.88a | 1.46b |
| ALG | 3.19b | 1.76b | 3.21a | 1.89ab |
| CMC | 3.79ab | 2.46ab | 3.00a | 1.68ab |
| PSY | 3.20b | 1.88b | 3.33a | 2.12a |
| LBG | 4.12a | 3.02a | 3.22a | 1.90ab |
| KGM | 3.75ab | 2.44ab | 3.31a | 1.99a |
| 0.8 % Addition level | | | | |
| Control | 3.67AB | 2.24AB | 2.88A | 1.46B |
| ALG | 4.11A | 2.68A | 3.24A | 1.81AB |
| CMC | 3.44AB | 2.00AB | 3.78A | 2.35A |
| PSY | 3.88AB | 2.57AB | 3.23A | 1.90AB |
| LBG | 3.10B | 1.78B | 3.33A | 2.01AB |
| KGM | 3.19B | 1.99AB | 3.09A | 1.89AB |

ALG=sodium alginate; CMC=carboxymethyl cellulose; PSY=psyllium husk powder; LBG=locust bean gum; KGM=konjac glucomannan

Means (n = 3) within a column with the same letter are not significantly different at the 5% probability level.

As a result, freezing endotherms were suppressed to a lower temperature range and water was removed from the freezable ('free') water pool resulting in relatively less ice formed in the subsequent freezing cycle. Similar depression effects on freezing endotherm T_o , T_p and ΔH values were seen on the other samples with food gums addition.

Technically, the extent of freezing parameters depression between freeze-thaw cycles could be used to determine the freeze-thaw stability of a frozen stored food system, this is more prominently shown in ΔH values. A lower magnitude in ΔH difference ($\Delta H_{1,2}$) between freeze-thaw cycles indicating a higher freeze-thaw stability. For control sample, frozen stored sample showed relatively higher $\Delta H_{1,2}$ than the fresh counterpart simply because with the absence of food gums more bound water molecules were released from wheat protein and starch molecules upon frozen storage. This results in an increase in freezable water (Sharadanant and Khan, 2003). It is interesting to note that among all fresh samples studied, only samples added with 0.2% and 0.8% ALG, 0.8% PSY showed a lower $\Delta H_{1,2}$ value than the control sample. Whereas, for all the frozen samples with food gums addition (0.2% and 0.8%), $\Delta H_{1,2}$ values were found to be lower than the control.

Table 3. Heat enthalpy, ΔH of freezing endotherm and melting endotherm of wheat flour dough with or without food gums added

| ΔH (J/g) of freezing endotherm | | | | | | |
|--|-----------|-----------|------------------|-----------|-----------|------------------|
| Sample | Fresh | | 2 months | | | |
| | 1st Cycle | 2nd Cycle | $\Delta H_{1,2}$ | 1st Cycle | 2nd Cycle | $\Delta H_{1,2}$ |
| 0.2 % Addition level | | | | | | |
| Control | 84.51b | 62.76a | 21.75 | 87.59a | 59.58b | 28.01 |
| ALG | 96.19ab | 75.28a | 20.91* | 92.55a | 74.35a | 18.20* |
| CMC | 92.33a | 68.48a | 23.85 | 93.36a | 72.77a | 20.59* |
| PSY | 94.09ab | 69.69a | 24.40 | 90.48a | 65.83ab | 24.65* |
| LBG | 90.96ab | 67.89a | 23.07 | 87.56a | 62.56b | 25.00* |
| KGM | 98.04a | 70.47a | 27.57 | 96.33a | 71.68a | 24.65* |
| 0.8 % Addition level | | | | | | |
| Control | 84.51B | 62.76B | 21.75 | 87.59AB | 59.58B | 28.01 |
| ALG | 91.99AB | 74.49A | 17.50* | 83.47B | 65.91AB | 17.56* |
| CMC | 89.17B | 65.66AB | 23.51 | 85.40AB | 64.68AB | 20.72* |
| PSY | 91.37AB | 71.88AB | 19.49* | 86.67AB | 69.71AB | 16.96* |
| LBG | 89.90B | 63.28B | 26.62 | 90.70AB | 71.17AB | 19.53* |
| KGM | 100.70A | 74.58AB | 26.12 | 97.32A | 72.80A | 24.52* |
| ΔH (J/g) of melting endotherm | | | | | | |
| Sample | Fresh | | 2 months | | | |
| | 1st Cycle | 2nd Cycle | $\Delta H_{1,2}$ | 1st Cycle | 2nd Cycle | $\Delta H_{1,2}$ |
| 0.2 % Addition level | | | | | | |
| Control | 94.68b | 80.04a | 14.64 | 99.06a | 78.96b | 20.10 |
| ALG | 105.92ab | 91.43a | 14.49* | 103.81a | 89.92a | 13.89* |
| CMC | 103.14b | 87.24a | 15.90 | 107.00 | 90.23a | 16.77* |
| PSY | 105.32ab | 89.52a | 15.80 | 103.08a | 85.23ab | 17.85* |
| LBG | 100.38ab | 86.67a | 13.71* | 96.96a | 81.90ab | 15.06* |
| KGM | 107.48a | 89.68a | 17.80 | 106.89a | 90.84a | 16.05* |
| 0.8 % Addition level | | | | | | |
| Control | 94.68B | 80.04B | 14.64 | 99.06A | 78.96B | 20.10 |
| ALG | 103.41AB | 88.98AB | 14.43* | 93.74A | 77.67B | 16.07* |
| CMC | 100.17B | 83.71AB | 16.46 | 96.56A | 79.76B | 16.80* |
| PSY | 102.88AB | 89.46AB | 13.42* | 98.37A | 86.12AB | 12.25* |
| LBG | 100.65B | 85.24AB | 15.41 | 101.66A | 87.41AB | 14.25* |
| KGM | 111.18A | 94.11A | 17.07 | 107.86A | 92.00A | 15.86* |

ALG=sodium alginate; CMC=carboxymethyl cellulose; PSY=psyllium husk powder; LBG=locust bean gum; KGM=konjac glucomannan; $\Delta H_{1,2}$ = difference in magnitude between 1st and 2nd freeze-thaw cycle. Means (n = 3) within a column with the same letter are not significantly different at the 5% probability level.

* The value is lower than the control samples.

This suggests that all food gums studied are able to stabilize frozen stored dough, in addition to increase the dough freeze-thaw stability. Based on the $\Delta H_{1,2}$ values obtained from the frozen stored samples, ALG showed the lowest $\Delta H_{1,2}$ value, indicating a strong cryostabilization effect. Results of Lee *et al.* (2002) revealed that sodium alginate showed good stabilizing effect on starch gel against freezing and thawing. The stabilizing effect of ALG can be ascribed to its ionic nature. The ionic groups of ALG will interact with the surrounding water molecules and restrict their mobility. Hence, there is difficulty for liquid water molecules to transform into ice crystals or to include into the association of polysaccharide chain (Sanderson, 1981; Lee *et al.*, 2002). Besides ALG, PSY and LBG at 0.8 % addition level were showing comparable cryostabilization effects as ALG.

Storability of frozen dough

According to Sharadanant and Khan (2003), lower freezing endotherm T_o and T_p values provides an indication of better storability of frozen dough because dough with lower freezing temperatures can be stored at a lower temperatures at which physical,

enzymatic and biochemical reactions are minimized.

Freezing endotherm T_o and T_p values of all fresh sample type for both addition levels were found to be not significantly different (Table 1 and Table 2). On the other hand, ΔH values of samples added with 0.2% and 0.8% KGM were significantly higher than the others. There means to say, these samples possess higher amount of freezable water. Similar trend in which there is an increment of freezable water upon food gums addition also reported by Rachel Crockett (2009) and Linlaud *et al.* (2011). Rachel Crockett (2009) studied the effects of high-methoxyl hydroxypropyl methylcelluloses (HPMC), low-methoxyl HPMC and xanthan gum on cassava rice dough at addition levels of 2, 3 and 5%. DSC analysis revealed that all the doughs added with hydrocolloids with the exception of dough added with 5% high-methoxyl HPMC showed significant greater amount of freezable water as compared to dough without hydrocolloid addition. In addition, Linlaud *et al.* (2011) evaluated the amount of freezable water for wheat doughs upon addition of hydrocolloids (xanthan gum, locust bean gum, guar gum, and high-methoxyl pectin). Freezable water showed an increase with the addition of hydrocolloids especially at constant hydration of dough, with the exception of dough added with high-methoxyl pectin. For doughs prepared at fixed water level and with the addition of hydrophilic hydrocolloids, a limitation in water available for freezing would be anticipated. However, the results showed a reverse trend and this could be attributable to the dough matrix binds water in a loosened way and cause an increase in freezable water (Linlaud *et al.*, 2011). An opposite result trend was reported by Sharadanant and Khan (2003), wherein a decrease of ΔH value was observed for dough added with food gums with the extent of decrease dependent on the addition levels of food gum.

As for frozen stored samples, there is no significant change in ΔH observed amongst samples studied of all type. When comparing ΔH value of fresh and frozen stored control sample, the value increase from 84.51 J/g to 87.59 J/g. However, the reverse is true for food gums added samples at both addition levels. This lower freezable water may consequently improve the frozen dough quality and the reason attributed to this observation was that the food gums help to bind water in dough. Sharadanant and Khan (2003) and Lu and Grant (1999) reported an increase in ΔH with increasing frozen storage time and a decrease in ΔH value after initial increase upon frozen storage, respectively. This discrepancy could be due to differences prevailed in dough formulations as well as preparation methods (Baier-Schenk *et al.*,

2005).

Melting endotherm

As shown in Table 1 and Table 2, melting endotherm T_o and T_p values of food gums added samples obtained after first freeze-thaw cycle were found to be insignificantly different when compared to the control sample. Same result trend was seen for the frozen stored samples. However, some significant differences were detected amongst frozen stored samples after being subjected to second freeze-thaw cycle. It is clearly seen that T_o value for samples added with 0.2% (ALG, CMC, PSY, LBG, KGM) and 0.8% (CMC) was lower than the control sample. As for T_p , only samples with 0.2% (PSY, KGM) and 0.8% (CMC) were significantly higher than the control counterpart. The plausible reason for this different trend in T_o and T_p was not clear. Obviously, all frozen stored samples with food gums addition (0.2% and 0.8%) showed relatively lower difference in melting enthalpy between the first and second freeze-thaw cycles. The same explanation as mentioned previously is applied.

Table 4 shows the midpoint glass transition temperature, $T_{g, \text{midpoint}}^*$ of dough samples. $T_{g, \text{midpoint}}^*$ was detected from the first derivative plot of the second scan (Tananuwong and Reid, 2004). Results in Table 4 show that for fresh sample addition of food gums at 0.2 % and 0.8 % was not significant in changing $T_{g, \text{midpoint}}^*$, except for sample added with 0.8% ALG, by which $T_{g, \text{midpoint}}^*$ significantly higher than the others. As for 2-month frozen stored samples, dough with food gums addition at 0.2% showed higher $T_{g, \text{midpoint}}^*$ than the control and $T_{g, \text{midpoint}}^*$ values between food gums added sample were not significantly different. When the food gums addition level was increased to 0.8%, same trend was observed with exception to sample added with 0.8% CMC, whereby $T_{g, \text{midpoint}}^*$ value became insignificantly different from the control counterpart.

Table 4. Midpoint glass transition temperature, $T_{g, \text{midpoint}}^*$ of wheat flour dough with or without food gums added

| Sample | Fresh | 2 months |
|-----------------------------|---------------------------------|---------------------------------|
| | $T_{g, \text{midpoint}}^*$ (°C) | $T_{g, \text{midpoint}}^*$ (°C) |
| 0.2 % Addition level | | |
| Control | -7.74a | -8.83a |
| ALG | -7.15a | -6.98b |
| CMC | -6.65a | -7.23b |
| PSY | -8.06a | -6.94b |
| LBG | -6.28a | -7.14b |
| KGM | -7.63a | -7.03b |
| 0.8 % Addition level | | |
| Control | -7.74AB | -8.83A |
| ALG | -5.46C | -6.18C |
| CMC | -9.16A | -8.87A |
| PSY | -6.52BC | -6.56BC |
| LBG | -7.98AB | -7.21B |
| KGM | -7.37AB | -7.16B |

ALG=sodium alginate; CMC=carboxymethyl cellulose; PSY=psyllium husk powder; LBG=locust bean gum; KGM=konjac glucomannan
Means (n = 3) within a column with the same letter are not significantly different at the 5% probability level.

It is commonly known that gums possess good water binding capacity as well as viscosity enhancing properties (Levine and Slade, 1986; Simatos and Blond, 1993; Wang *et al.*, 1998). Therefore, the cryostabilizing effects of food gums could be attributable to its capability in limiting molecular mobility and hence controlling diffusion controlled reactions such as crystallization (Torreggiani *et al.*, 1999; Herrera *et al.*, 2007). Study of Simatos *et al.* (1995) revealed that polysaccharides limit molecular mobility by increasing T_g' , this resulting in a slower ice crystal growth rate when the sample was kept at a temperature above T_g' (Simatos *et al.*, 1995; Lopez *et al.*, 2005). Maity *et al.* (2011) reported that hydrocolloids such as pectin, carboxymethylcellulose, xanthan gum and sodium alginate were found to significantly increase T_g' of frozen-thawed pre-cut carrots and T_g' was increased with increasing concentration of hydrocolloids. In addition, hydrocolloid treatments were shown to help in reducing the drip losses and gave better texture and sensory acceptability to the samples. Results of Goff *et al.* (1993) showed that polysaccharides stabilizers were able to give protective effect on the ice crystals growth to ice cream mixes upon thermal deformation and enhanced subzero viscosity above the T_g' but did not affect the thermal properties. This may ascribe to the alteration of the diffusion properties within the unfrozen phase (Goff, 1995).

Dynamic Mechanical Analysis (DMA)

Stability of food during frozen storage is dependent on the molecular mobility of unfrozen phase which affects the physical and chemical alterations (Torreggiani *et al.*, 1999; Liu *et al.*, 2006; Maity *et al.*, 2011). According to Slade and Levine (1991), it is proposed that frozen foods are stable when being stored at temperature below its sub-zero glass transition temperature, T_g' as maximally freeze-concentrated state is achieved. In order to achieve long-term stability of a frozen product, food formulation can be modified by elevating the glass transition temperature above the storage temperature (Kobs, 1997; Torreggiani *et al.*, 1999). When T_g' is below the storage temperature, this increases mobility in a frozen food system and promotes water migration as well as growth of ice crystals (Kobs, 1997). It is suggested that food gums are able to serve as a cryostabilizer which can increase T_g' of food system due to its high molecular weight and its hygroscopicity to bind water. In addition, viscosity enhancing properties of food gums causes slow diffusion in unfrozen phase and thus hinders ice crystals growth in a food matrix (Goff, 1992).

Figure 1 depicts a typical DMA thermogram of dough sample. In general, dough is seen to become less stiff as a function of temperatures resulting in a gradual decrease in storage modulus (G'). This indicates that the dough becomes softened over the glass transition temperature area (Perkin Elmer, 2007). Three peaks have been observed in the loss modulus (G'') curve. As reported by Ribotta and Le Bail (2007), the peaks were corresponded to ice melting temperature (T_m), α -transition temperature (T_g'), and β -transition temperature (T_g''), respectively. The T_g' values detected in dough samples were summarized in Table 5.

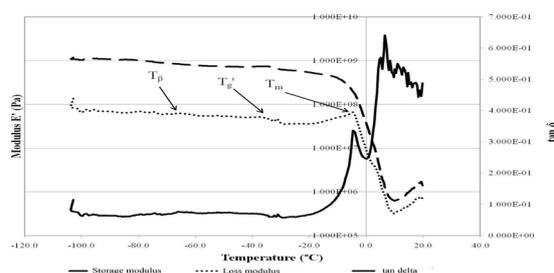


Figure 1. Typical DMA thermogram

Table 5. Sub-zero glass transition temperature, T_g' of frozen wheat flour dough with or without food gums added

| 0.2% Addition level | | | 0.8% Addition level | | |
|---------------------|-------------|-----------------|---------------------|-------------|-----------------|
| Sample | T_g' (°C) | ΔT (°C) | Sample | T_g' (°C) | ΔT (°C) |
| Control | -38.4b | 20.4 | Control | -38.4B | 20.4 |
| ALG | -29.1a | 11.1 | ALG | -32.2AB | 14.2 |
| CMC | -32.5a | 14.5 | CMC | -31.5A | 13.5 |
| PSY | -27.3a | 9.3 | PSY | -31.4A | 13.4 |
| LBG | -28.7a | 10.7 | LBG | -37.3AB | 19.3 |
| KGM | -30.6a | 12.6 | KGM | -34.2AB | 16.2 |

At 0.2 % level, T_g' of all dough samples with food gums added showed elevated T_g' values as compared to the control sample ($P < 0.05$). However, insignificant difference was shown between food gums added samples. Whereas, at 0.8% level, only CMC and PSY added samples significantly increase T_g' value of wheat dough when compared to the control sample ($P < 0.05$). From the results tabulated in Table 5, the difference between T_g' and practical frozen storage temperature (-18°C) becomes smaller with the addition of food gums at both addition levels.

The discrepancy between $T_{g,\text{midpoint}}^*$ value determined by DSC and T_g' value obtained by DMA might be attributable to different sample preparation method (Räsänen *et al.*, 1998). In DSC analysis, glass transition temperature is determined based on heat flow change, a function of the kinetic variation in the temperature. As for DMA, glass transition temperature is detected from a function of the

frequency in which the mechanical properties and energy loss of sample are measured. In addition, different heating profiles were used in both type of thermal analysis measurements (Lopez *et al.*, 2005).

Results in the present study revealed that food gums are not very effective in raising the T_g' of a food system until above the practical frozen storage temperature (-18°C) but is able to bring the temperature difference between sample T_g' and storage temperature closer. According to Levine and Slade (1988, 1990), when a frozen matrix is being stored at temperature above its T_g' , the reaction kinetics at molecular level are mainly governed by the temperature difference between the storage temperature and the T_g' of the food product ($\Delta T = T_s - T_g'$) as stated in Williams-Landel-Ferry kinetic theory. The quality deterioration of a food product is related to the temperature difference between the storage temperature and the T_g' , in which greater quality loss occurred in conjunction with the greater temperature difference (Lim *et al.*, 2006). Hence, a better frozen dough stability could be anticipated with food gums addition.

Conclusion

Addition of food gums plays a role in modifying ice crystallization and melting properties of a frozen wheat dough at sub-zero temperature. This is mainly attributed to the fact that food gums are good water binder and capable of controlling water molecules migration in food matrix. In other words, storage stability of frozen dough can be enhanced with addition of food gums.

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