

Thai creamed honey: enthalpy of crystal melting and texture profile under different storage conditions

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Abstract

The effects of different storage conditions of Thai creamed honey on the texture profile and thermodynamic properties were successfully investigated by using the differential scanning calorimetry (DSC) method. Liquid and creamed sunflower, longan, and wild honey were analysed in the present work due to Thailand's large production capacity. The glass transition temperature (T_g) and enthalpy of sugar fusion (ΔH_f) exhibited insignificant differences between liquid and creamed honey. Only the enthalpy of crystal melting (ΔH_m) was an indicator to distinguish the phase of honey, since it was imperceptible for liquid honey in the melting temperature ranging between 30 - 60°C. In addition, the correlation between hardness values and ΔH_m can be a new parameter to obtain the best texture of Thai creamed honey at chilled temperature during storage.

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Introduction

Honey is composed of various sugars, and a supersaturated solution at normal temperatures due to the glucose content. Glucose and fructose are the main sugars in honey, while sucrose and maltose are present in little amounts. Glucose and fructose in honey are approximately 33 – 35% and 38 – 40%, respectively, and their total content is above 65% (w/w) of honey. Usually, fructose content is almost higher than that of glucose (Bhandari *et al.*, 1999). During honey crystallisation, glucose, which is the least soluble component of all sugars in honey, crystallises when the glucose-monohydrate forms under certain conditions. Honey crystallisation is an undesirable in processing, handling, and marketing, and it is an unacceptable characteristic for consumer satisfaction.

However, this property may be desirable for a particular purpose such as creamed honey production. Nevertheless, it is not easy to control the process, especially with various honey types in Thailand, without studying their physicochemical and thermal properties. According to the Department of Agriculture Extension, Ministry of Agriculture and Cooperatives of Thailand, Thai honey production in 2019 was over 10,000 t, 70% of which were exported, and there are three types (sunflower, longan, and wild honey) which have large production capacity in

Thailand, thus cannot be sold at a high price. Therefore, the creamed honey product is an exciting product to increase their market value for honey entrepreneurs.

In terms of crystallised or creamed honey, liquid honey takes a semisolid state when the sugar concentration is high. The rate of crystallisation depends on many factors such as the presence of crystallisation nuclei, the concentration of sugars that may crystallise, and the storage temperature. Moreover, centrifuge and pumps produce small air bubbles or seeding addition which affects the tendency of the product to crystallise (Mora-Escobedo *et al.*, 2006). This is an undesirable process, and may cause a gritty texture of creamed honey. Cream honey with a good texture spreads like butter, and it should not drip, which can be obtained from the proper process to control the crystallisation. Thus, an attempt to determine specific precautions to control crystallisation in creamed honey should be investigated.

Many authors have reported the change in physicochemical and thermodynamic properties due to honey crystallisation (Lupano, 1997; Conforti *et al.*, 2006; Venir *et al.*, 2010; Dettori *et al.*, 2018), and many reports attempted to evaluate adulteration of honey by changing the enthalpy using differential scanning calorimetry (Cordella *et al.*, 2003; Sobrino-Gregorio *et al.*, 2017). Differential scanning

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calorimetry (DSC) is an alternative analytical technique, and a relatively fast, cheaper, and environmentally friendly technique to differentiate genuine from adulterated honey. Lupano (1997) studied the melting enthalpy values using DSC, and found that it was an appropriate tool to analyse the honey granulation. Besides, Tomaszewska-Gras *et al.* (2015) used DSC to investigate thermal processes in crystallised honey. DSC can be used to study most physical or chemical transformations involving heat exchanges; therefore, DSC has a very broad field of application. Even when no heat exchange occurs as observed in glass transitions, the phenomenon causes a baseline deviation of the thermoanalytical curve related to a change in heat capacity. Moreover, DSC is a powerful tool to address the most challenging issues in glass science and technology such as kinetics of glass-forming systems during crystallisation (Jaturonglumert and Kiatsiriroat, 2010; Zheng *et al.*, 2019). Glass transition and enthalpy measurement provide detailed information about the physical and energetic properties of a substance (Cordella *et al.*, 2002), and DSC is suitable to determine the real nature of phase transitions, and reveals the occurrence of thermal events. However, to our knowledge, there are very few works which studied about creamed honey product, and data of the thermodynamic properties to distinguish between liquid and creamed honey, and correlate them with the product appearance have not been published.

The consistency or texture of the final structure in creamed honey depends on the composition of the starting honey and storage temperature (Hempattarasuwan *et al.*, 2019). The temperature affects the viscosity of honey: high temperature may make the creamed honey return to the liquid form during storage, or the final hardness may vary at different storage temperatures. Therefore, the texture variation, *e.g.*, firmness, hardness, and adhesiveness during storage should be monitored in various storage conditions to further design the optimal storage condition and to determine the product's shelf-life.

The present work investigated the thermodynamic and texture properties of creamed honey, which will fill the knowledge gap and provide useful data for honey processors. Different storage conditions that affect the enthalpy value in the melting transition and texture profile were also investigated.

Materials and methods

Raw materials and sample preparation

Sunflower, longan, and wild honey (fresh and non-crystallised honey) were purchased from Supha Bee Farm, Chiang Mai province, Thailand. Samples of 100 g were heated at 50°C to eliminate natural crystals and osmotolerant/osmophilic yeasts using a water bath. Heated honey samples were cooled to room temperature, and stored in labelled glass containers at 27 - 30°C (average temperature in Chiang Mai province, Thailand from January to March 2020). The samples were further analysed for physicochemical and thermal properties.

Creamed honey preparation

Three types of creamed honey samples were prepared following previous research (Suriwong *et al.*, 2020) by developing them using Dyce's method (Abou-Shaara and Elhamid, 2017). Liquid honey was heated with ultrasonic treatment at 50°C, and rapidly cooled to 20°C. Then, seed honey was added with slow agitation at 100 - 300 rpm for 5 min. The seed honey was prepared from a previous batch of creamed honey preliminary test, and it was separated by each honey type to prevent cross contamination. Next, the thoroughly mixed honey was filled into glass containers, sealed, and kept at 4 - 10°C (chilled temperature). The creamed honey samples remained at chilled temperature for one week prior to being stored at different temperatures (chilled and room temperature), in different storage times (7, 14, 21, and 30 days) to further analyse the physicochemical, thermodynamic and textural properties. Commercial airborne Manuka and Wildflower cream honey from New Zealand were purchased from a supermarket in Chiang Mai province to compare their textures with the laboratory creamed honey.

Sugar analysis

The sugar compositions (glucose, fructose, maltose, and sucrose) of honey samples were determined by HPLC (Agilent, USA) based on method 977.20 (AOAC, 2000). The honey solution was filtered through a 0.45- μ m filter, and immediately injected into an HPLC fitted with a refractive index (RI) detector. The HPLC column was a μ -Bondapak carbohydrate column with 4-mm diameter and 300-mm length, and it was operated with the eluting solvent of acetonitrile:water at a ratio of 87:13. The sugars' content in the honey samples was calculated using a standard calibration curve. The moisture and sugar contents of the liquid and creamed honey samples (sunflower, longan, and wild honey) were measured before analysing their thermal properties. The moisture content was determined using an Abbe refractometer (KRUSS, Germany).

Three samples from each trial were analysed for moisture determination, and the average moisture content was reported.

Differential scanning calorimetry analysis

A Mettler-Toledo DSC 1 Module with the STARE software (Mettler-Toledo) was used to investigate honey samples' thermal behaviour. Indium and zinc standards were used to calibrate the differential scanning calorimeter, and the measuring range was extended to -65°C by a cooling Intra Cooler system. A calorimetric heat flow was used to obtain quantitative and qualitative data concerning the net heat changes produced by carbohydrates during their heating. Honey samples (10 mg) were placed in a weighed aluminium DSC hermetic pans, and as a reference, an empty crucible was simultaneously measured. The experiments were conducted from -65 to 200°C to obtain the complete thermal behaviour of pure and creamed honey from low to high temperature. All samples were subjected to the following temperature cycle: from 25 to -65°C , from -65 to 200°C , and held for 5 min. Various start temperatures and heating rates were applied to the samples following the previous literature reports (Cordella *et al.*, 2002; 2003; Tomaszewska-Gras *et al.*, 2015). After evaluating the effect in the range of 2 - $50^{\circ}\text{C}/\text{min}$, we selected a heating rate of $10^{\circ}\text{C}/\text{min}$. The calorimetric response improved this heating rate without a decrease in accuracy, reduced the analysis time, and decreased sample degradation risk. Three DSC runs were performed to determine various glass transition temperatures (T_g) and the samples' melting behaviour at higher temperatures to calculate the enthalpy of crystal melting (ΔH_m , J/g) and enthalpy of sugar fusion (ΔH_p , J/g).

Textural analysis

Measurement was made with the TA.XT-PLUS Texture Analyser (Stable Micro Systems Ltd., UK). Test parameters were selected based on preliminary trials. A conical probe P/60C was used to penetrate a creamed honey samples to a 10-mm depth at a rate of 10 mm/s. For each sample, three replicates were analysed at each sampling time. The acquired curves of Force (N) versus time (s) shows the hardness (N) as the maximum force at the positive highest peak, and the adhesiveness (N.s) as the maximum negative force area after compression.

Statistical analysis

Results were expressed as mean \pm standard deviation (mean \pm SD) of a triplicate test, as an independent experiment. Analysis of variance

(ANOVA) was used for statistical analysis, followed by Duncan's multiple range test (DMRT). The significant difference of responses at $p \leq 0.05$ was analysed by Duncan's method, and statistical processing was performed using SPSS 17.

Results and discussion

Characterisation of liquid and creamed honey

The three honey types had different compositions (Table 1) due to the floral source, climate, and environmental conditions. Pure sunflower honey had the highest glucose content which was $37.05 \pm 4.290\%$, higher than longan and wild honey which were 32.82 ± 0.911 and $31.58 \pm 0.494\%$, respectively. Sucrose (0.26 - 0.82%, w/w) and maltose (0.16 - 1.44%, w/w) were present in very small amounts in these samples. Moreover, as shown in Table 1, the fructose to glucose ratio (F/G ratio) of liquid sunflower honey was 1.09, which was less than 1.14 (Venir *et al.*, 2010). This strongly showed that sunflower honey could initiate rapid crystallisation. The values of longan and wild honey (1.24 and 1.22, respectively) could be associated with slow or no tendency to crystallise. Therefore, it was expected that the composition of liquid honey would change after a creamed honey product was produced by controlling the crystallisation process. In addition, the sample with the highest glucose content had the lowest moisture content for both liquid and creamed honey samples. The glucose to water ratio (G/W ratio) used as an indicator of crystallisation was 1.63 - 2.05 (the liquid honey sample with the highest moisture content was wild honey, and the lowest moisture content was sunflower honey). Bhandari *et al.* (1999) reported that honey samples with G/W ratio above 2.16 had fast crystallisation, while values below 1.70 indicated that the honey samples could remain as liquid for a long time. Therefore, it was expected that the creamed sunflower honey would crystallise the fastest and have the highest consistency during storage. The seed addition and vigorous mixing in creamed honey production are the main factors that affect the rate of crystallisation and consequently the fine texture in creamed honey. Primary glucose microcrystals, wax, and other insoluble particles can act as catalytic factors and be naturally present. These are also called nucleation seed or primers (Dettori *et al.*, 2018). When crystallisation occurs in a controlled manner, it is possible to have products such as creamy honey.

To study the crystallisation process, creamed honey samples were prepared by changing honey

from liquid to solid with the addition of seed as a stimulating nuclei. All creamed honey samples had mild flavour and spread like butter, unlike liquid honey. They did not drip, and also had a creamy texture. Creamed sunflower and wild honey had lighter yellow colour and tighter texture than creamed longan honey. In most cases, the texture was smooth and creamy, and there was no gritty sugar; this was similar to a commercial creamed honey product.

The compositions of creamed sunflower, longan, and wild honey are also presented in Table 1. The glucose content increased from the liquid state in all honey types, while the moisture content decreased. Regarding the creamed honey, it was a honey product obtained from the control of honey crystallisation, and crystallisation in honey is a natural phenomenon that happens when glucose spontaneously precipitates out of the supersaturated honey solution. After that, the glucose loses water (becoming glucose monohydrate), and takes the form of a crystal (a solid body with a precise and orderly structure). Therefore, the glucose and water contents between liquid and creamed honey samples were different. The F/G ratios of all creamed honey samples were less than those of liquid honey samples for all types; longan, wild, and sunflower honey had F/G ratios of 1.14, 1.08, and 0.97, respectively. A lower F/G ratio corresponds to a higher crystallisation rate and more crystallised honey (Bhandari *et al.*, 1999). Similarly, the G/W ratios were 2.16, 1.82, and 1.71 for creamed sunflower, longan, and wild honey, respectively, and increased in the liquid honey samples. Therefore, the crystallisation process can be controlled by changing the honey composition. A higher glucose concentration by seed addition can consistently initiate the crystallisation in honey to obtain the creamed honey sample's smooth texture.

Thermograms of honey

The thermograms of liquid and creamed honey samples depicted in Figure 1 show two and three thermal phenomena in most cases, respectively.

First thermal phenomenon (I)

In the first phase, *i.e.*, glass transition, a peak appeared in the range of -50 to -30°C . A glass transition can be observed at low temperatures when the material is not sufficiently ordered to crystallise. Therefore, amorphous material such as honey can be characterised by their glass transition temperature (T_g). This phenomenon is observed in well-known honey-like polymers (Cordella *et al.*, 2002). The T_g of the liquid and creamed honey samples were determined in the heating scan as the onset temperature. The liquid sunflower honey (-45.45°C) had significantly different T_g as compared to others (longan and wild honey of -48.48 and -48.95°C , respectively) (Table 2). In most cases of creamed honey samples, the T_g were not different among honey types: -48.30 , -48.55 , and -49.37°C . The report's range of T_g was from -49.50 and -42.0°C , which is similar to other honey types in many reports, -49.7 to -34.8°C and -45 to -39°C (Cordella *et al.*, 2002; Tomaszewska-Gras *et al.*, 2015). Thus, when the material changes from the rubbery state into the rigid, glassy state upon cooling or conversely from the glassy solid to the rubbery state upon heating, the glass transition occurs. From this result, T_g was not different between liquid honey and creamed honey; thus, T_g cannot be used to monitor the crystallisation process or the change in crystallisation behaviour.

Second thermal phenomenon (II)

An endothermic peak appeared in the temperature range of $30 - 60^{\circ}\text{C}$, which is the crystal melting transition. In Figure 1A, the peak is not present in all liquid honey samples because a peak in the thermograms corresponds to the melting of

Table 1. Composition (g/100 g) of liquid and creamed honey samples.

Sample	Glucose	Fructose	Sucrose	Maltose	Water	F/G ratio	G/W ratio
SU	37.05 ± 4.290	40.51 ± 0.216	0.54 ± 0.091	1.44 ± 0.091	18.00 ± 0.250	1.09	2.05
LG	32.82 ± 0.911	40.78 ± 2.737	0.75 ± 0.006	0.67 ± 0.001	18.58 ± 0.382	1.24	1.77
WD	31.58 ± 0.494	38.60 ± 0.474	0.82 ± 0.025	0.35 ± 0.001	19.42 ± 0.520	1.22	1.63
CR-SU	38.30 ± 0.033	37.25 ± 0.216	0.63 ± 0.031	0.16 ± 0.050	17.75 ± 0.289	0.97	2.16
CR-LG	33.06 ± 0.029	37.74 ± 0.021	0.41 ± 0.015	0.19 ± 0.009	18.17 ± 0.289	1.14	1.82
CR-WD	32.20 ± 0.018	34.67 ± 0.010	0.26 ± 0.006	0.19 ± 0.007	18.83 ± 0.144	1.08	1.71

Values are mean \pm SD of three replicates ($n = 3$). SU: liquid sunflower honey; LG: liquid longan honey; WD: liquid wild honey; CR-SU: creamed sunflower honey; CR-LG: creamed longan honey; and CR-WD: creamed wild honey.

Table 2. Transition temperature (T_{onset} , T_{midpoint}), enthalpy of crystal melting (ΔH_m), peak of temperature (T_{peak}), and enthalpy of sugar fusion (ΔH_f) of liquid and creamed honey samples.

Sample	Thermal phenomena					
	Glass transition (T_g)		Crystal melting		Fusion of sugars	
	T_{onset}	T_{midpoint}	T_{onset}	ΔH_m	T_{peak}	ΔH_f
SU	-45.45	-42.23	N	N	134.83	171.240 ± 0.547 ^a
LG	-48.48	-45.04	N	N	124.67	199.303 ± 1.130 ^b
WD	-48.95	-45.17	N	N	132.80	221.577 ± 3.376 ^c
CR-SU	-48.30	-44.49	27.78	2.140 ± 0.010 ^c	133.83	171.607 ± 0.349 ^a
CR-LG	-48.55	-45.09	27.43	0.613 ± 0.006 ^b	130.50	224.170 ± 0.209 ^b
CR-WD	-49.37	-45.96	27.60	0.033 ± 0.002 ^a	136.83	226.350 ± 0.568 ^c

N = not measured due to absence; T_{onset} , T_{midpoint} , and T_{peak} are in °C; H are in J/g; SU: liquid sunflower honey; LG: liquid longan honey; WD: liquid wild honey; CR-SU: creamed sunflower honey; CR-LG: creamed longan honey; and CR-WD: creamed wild honey.

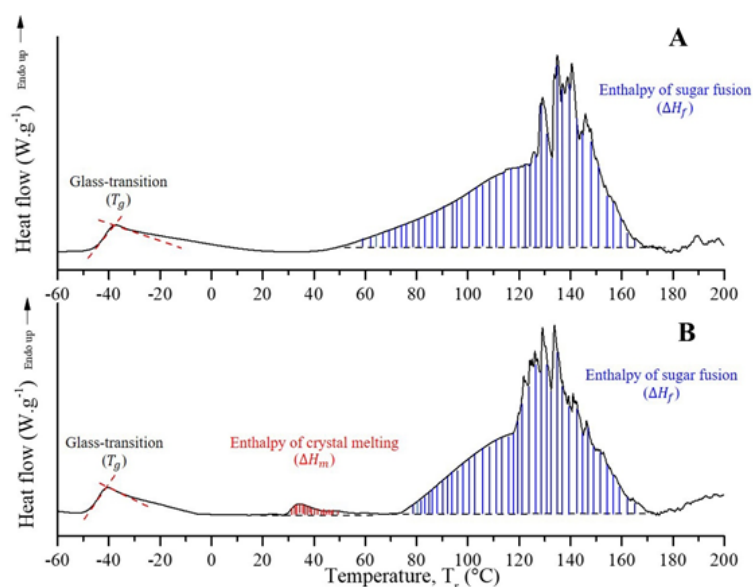


Figure 1. An example of DSC scan of (A) liquid, and (B) creamed sunflower honey in temperature range of -65 to 200°C, and heating rate 10°C/min.

crystals in honey. There was no crystal in pure sunflower, longan, and wild honey, while the creamed honey samples consisted of glucose crystals. The enthalpy of melting (ΔH_m) was computed from the area of the endothermic peaks in the range of 30 - 60°C, so the more granulated the honey was, the greater the recorded area. A higher glucose content corresponds to a higher enthalpy of crystal melting. Creamed sunflower honey had the highest enthalpy (ΔH_m) of 2.140 ± 0.010 J/g due to the highest glucose content (38.30%). According to Lupano (1997), more granulated honey crystals are present with a greater peak area, and more activation energy is required to melt the crystals. Therefore, the low-temperature storage and seeding addition during the creamed honey processing may initiate the nucleation process, since sugar molecules have sufficient mobility to form a crystal lattice, and the

peak was observed after seven days of storage.

Final thermal phenomenon (III)

Both liquid and creamed honey samples showed a very wide and intense endothermic peak in the temperature range of 100 - 170°C, which is called the transition of sugar fusion. The fusion temperature of the sugars in liquid and creamed honey begun at 83.68 - 118.22°C and ended at 147.31 - 168.67°C, depended on the thermal history of the samples. This peak is similar to that in Tajonal honey reported by Mora-Escobedo *et al.* (2006) who observed that this peak indicated a particular composition of Tajonal honey. The observed peak in Tajonal honey samples began at 93 - 123°C and ended at 140 - 175°C (Mora-Escobedo *et al.*, 2006). Therefore, these confirmed that this range's peak represented the enthalpy in the melting process of sugar in honey.

The liquid and creamed honey samples did not have a different enthalpy of sugar melting (ΔH_f) such as mono-, di-, tri-, and oligosaccharides. The range of the sugar-melting enthalpy was 171.24 - 226.35 J/g. Cordella *et al.* (2003) showed the enthalpies of sugars fusions in *Lavandula*, *Robinia*, and *Fir* honey at 256.2, 213.1, and 228.9 J/g; this value did not appear as the most appropriate parameter to distinguish floral species or sugar content. However, it was essential for detecting adulteration in honey because adulterated honey has the highest enthalpies of sugar fusions. Therefore, the change in enthalpy of crystal melting (ΔH_m) is a proper parameter to study the crystal variation of creamed honey, and could be used to find the relation with the changes in texture during storage.

Thermograms of creamed honey stored in different conditions

Thermograms of creamed sunflower, longan, and wild honey in the range of crystal melting (30 - 60°C), stored at chilled and room temperature, are shown in Figure 2. The recorded area under the endothermic peak was observed to study the change in enthalpy of crystal melting in different storage conditions. In most types of creamed honey samples, when the storage time increased, the recorded area of the peak widened during storage at chilled temperature (Figures 2A - 2C). The endothermic

peaks are due to the melting of glucose crystals, and their integration shows the relative melting enthalpy. Thus, the honey crystal dissolved, and the enthalpy of crystal melting decreased during storage.

Enthalpy values ΔH_m (J/g) obtained by integrating the endothermic peaks only provide information about the total amount of crystallised sugar, but not the crystal dimensions. Figure 2 shows the change in enthalpy of crystal melting (ΔH_m) with storage time. The area under the peak or ΔH_m of creamed sunflower honey increased with storage time at chilled temperature (Figure 2A), but decreased at room temperature (Figure 2D). ΔH_m in creamed sunflower honey increased from 4.98 J/g (day 1) to 21.14 J/g (day 30); similarly, ΔH_m was 0.61 J/g (day 1) and 4.66 J/g (day 30) for creamed longan, and 0.032 J/g (day 1) and 19.04 J/g (day 30) for wild honey (Figures 2B and 2C). The enthalpy value represents the amount of heat needed to melt crystals present in honey; the amount of crystallised sugar increased when the time of the chilled storage increased, so the energy used in melting the crystals also increased. This fact is consistent with Lupano (1997) who showed that the enthalpy of polyfloral honey rapidly increased when stored at 4 and 10°C, whereas the samples stored at 20°C presented a slower increase.

The peak of creamed longan and wild honey decreased in area and sharpened when the storage

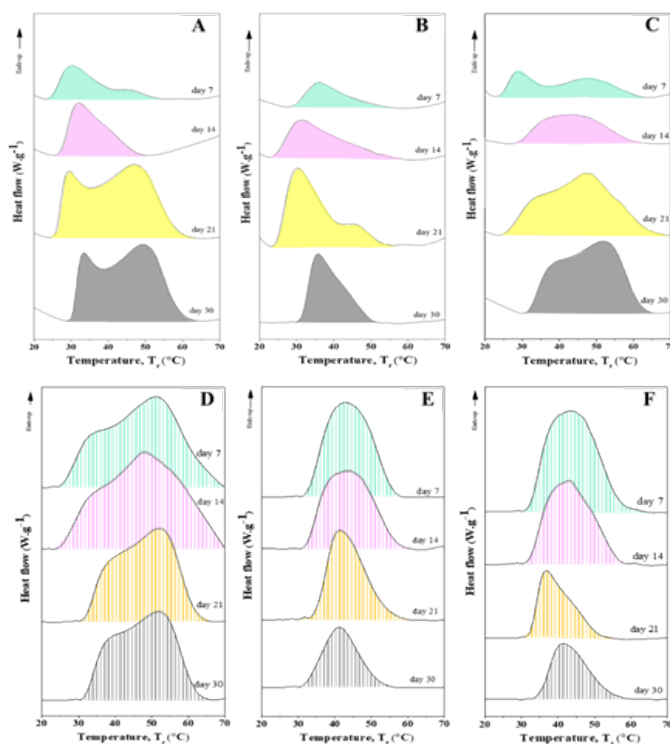


Figure 2. DSC thermograms of creamed honey stored at chilled (A) - (C) and room (D) - (F) temperatures. Creamed honey type: (A) and (D) sunflower honey; (B) and (E) longan honey; (C) and (F) wild honey.

time increased at room temperature (Figures 2E - 2F). Similarly, creamed longan and wild honey appeared liquid during room temperature storage, which implied that their consistency decreased when the storage time increased. ΔH_m in creamed wild honey was 13.56 and 6.68 J/g_m on day 1 and 30, respectively, which decreased when the storage time increased. This result is similar to the report of Zamora and Chirife (2006) and Costa *et al.* (2015) in which the solubility of glucose increased, and the tendency to crystallise was low when the temperature increased. This also explains the slow crystal growth in all types of honey at 25°C (Nurul Zaizuliana *et al.*, 2017).

Texture of creamed honey stored in different conditions

Regarding the crystallisation variation and textural properties that may change with temperature, to evaluate the spreadability of creamed honey at various storage temperatures, textural studies were performed to obtain the parameters of hardness (N) and adhesiveness (N.s).

Figure 3 shows the change in hardness and adhesiveness of creamed honey samples at different storage conditions. The hardness involves the maximum force during compression (Shinn and Wang, 1990), and the adhesiveness is the maximum negative force registered during upstroke. The creamed samples' initial hardness was 9.28 - 13.53 N, and not linearly related to the adhesiveness. Hardness increased when the storage time increased, and

proportionally increased with the rate of crystallisation and amount of crystallised glucose (Dettori *et al.*, 2018). The crystallisation rate in previous work depended on the glucose content, and rapidly increased in sunflower honey (Suriwong *et al.*, 2020). The hardness of creamed sunflower honey rapidly increased when the storage time increased at chilled temperature, while it slowly increased for creamed longan and wild honey (Figure 3A). The hardness of creamed honey can be considered an index of the internal forces in the structure of creamed honey; the values were 115.42, 48.22, and 26.31 N for creamed sunflower, longan, and wild honey, respectively. Creamed sunflower honey presented more rigid, tighter, and harder texture than creamed longan and wild honey. The solid texture effect was due to a much greater amount of glucose. The results showed that the composition influences the rate of crystallisation, and the amount of glucose that crystallises also affects the final structure, and consequently, the textural properties. Thus, a larger force is required for the first compression when the crystal formation increases during storage at low temperature; *i.e.*, the crystalline phase increases, and a solid structure is formed where the crystals create a matrix, which is characterised by a cohesion that increases with time.

The hardness slowly changed at room temperature for creamed sunflower honey, but rapidly decreased for creamed longan and wild honey, which appeared more liquid or returning to the liquid form. The hardness value decreased from

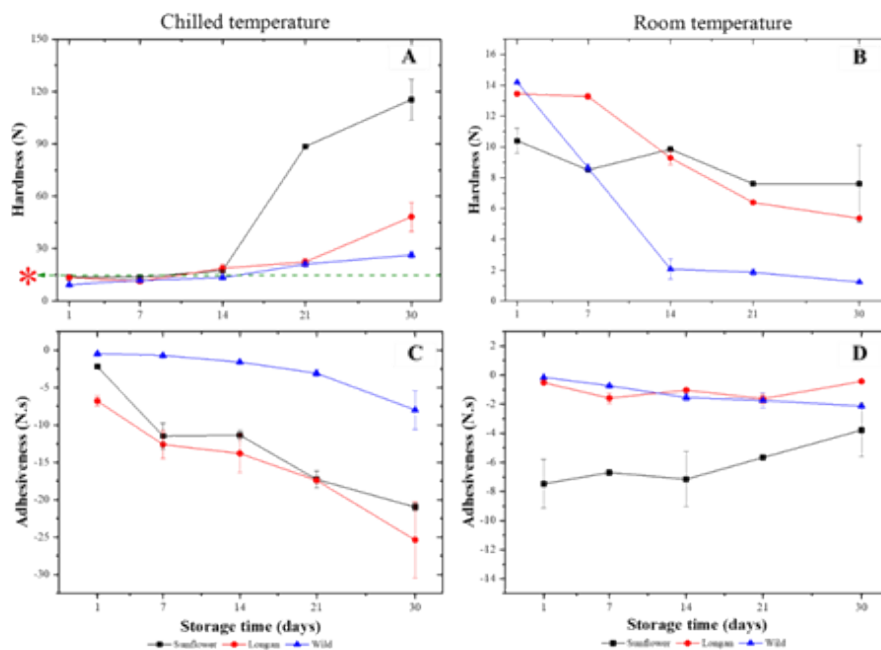


Figure 3. Textural parameters of (A - B) hardness, and (C - D) adhesiveness of creamed sunflower, longan, and wild honey samples stored at chilled and room temperatures.

14.25 N (day 1) to 1.23 N (day 30), as shown in Figure 3B. The adhesiveness decreased when the storage time increased (Figure 3C), but not clearly in the storage condition of room temperature (Figure 3D). Karasu *et al.* (2015) explained that this phenomenon based on the thermal loop test method: creamed honey had low thermal stability, and abstained from large temperature fluctuations. They suggested that the crystallised or creamed honey should be kept at a temperature below 40°C to avoid irreversible changes in rheological or textural characteristics to maintain spreadability, especially for creamed longan and wild honey.

Correlation between ΔH_m and hardness

The creamed honey in the laboratory should present a smooth texture similar to the commercial product, and the texture of the commercial product was measured to compare with our creamed honey samples. The commercial airborne Manuka and Wildflower cream honey product was selected to represent the smooth texture product from the market, and the hardness was 14.971 ± 0.202 N (green line in Figure 3A). The hardness values of creamed sunflower, longan, and wild honey were 17.382 ± 0.306 , 18.685 ± 2.571 , and 13.382 ± 0.624 N, respectively, on day 14, and the product had the best firmness and high consistency at chilled temperature. Since the hardness increased with longer storage time, so the product was harder at chilled temperature and was not spreadable. Since these values were close to the commercial product's hardness value, our creamed honey samples are acceptable to consumers. There was a correlation between ΔH_m and hardness: the hardness and ΔH_m increased when the samples were kept at a chilled temperature. On day 14, ΔH_m were 3.673, 2.247, and 2.957 J/g for creamed sunflower, longan, and wild honey, respectively, at chilled temperature. Therefore, to determine the optimal ΔH_m of Thai creamed honey, the acceptable value of hardness can be used to estimate the enthalpy of crystal melting in creamed honey. However, honey properties and type should also be considered.

Conclusion

Thermograms obtained by differential scanning calorimetry could be used to study the thermal properties of creamed honey in the present work. The enthalpy value of crystal melting (ΔH_m) could be an indicator to distinguish different phases of honey, which were imperceptible in liquid honey in the melting temperature ranging between

30 - 60°C. T_g and the enthalpy of sugar fusion (ΔH_f) did not significantly vary for different honey types. The storage condition affected the enthalpy of crystal melting and texture properties, especially the hardness. Creamed sunflower honey could be stored at both chilled and room temperatures because it did not show a decrease in enthalpy, and the hardness did not significantly change during storage. Meanwhile, the hardness of creamed longan and wild honey decreased during storage at room temperature. The hardness of creamed honey involved the consistency of creamy texture during storage; so, creamed longan and wild honey should not be stored at room temperature to prevent the creamed honey from returning to the liquid form. The positive correlation between hardness and ΔH_m could be used to obtain the best texture of the final product.

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References

- Abou-Shaara, H. and Elhamid, A. 2017. Effects of nuclei type on characteristics of creamed honey. *Journal of Apiculture* 32(1): 59-62.
- Association of Official Analytical Chemists (AOAC). 2000. Sugars and sugar products: separation of sugars in honey. In *Official Methods of Analysis of AOAC* (17th ed). United States: AOAC.
- Bhandari, B., D'Arcy, B. and Kelly, C. 1999. Rheology and crystallisation kinetics of honey: present status. *International Journal of Food Properties* 2(3): 217-226.
- Conforti, P. A., Lupano, C. E., Malacalza, N. H., Arias, V. and Castells, C. B. 2006. Crystallisation of honey at -20°C. *International Journal of Food Properties* 9(1): 99-107.
- Cordella, C., Antinelli, J.-F., Aurieres, C., Faucon, J.-P., Cabrol-Bass, D. and Sbirrazzuoli, N. 2002. Use of differential scanning calorimetry (DSC) as a new technique for detection of adulteration in honeys. 1. Study of adulteration effect on honey thermal behavior. *Journal of Agricultural and Food Chemistry* 50(1): 203-208.

- Cordella, C., Faucon, J.-P., Cabrol-Bass, D. and Sbirrazzuoli, N. 2003. Application of DSC as a tool for honey floral species characterisation and adulteration detection. *Journal of Thermal Analysis and Calorimetry* 71(1): 279-290.
- Costa, L. C. V., Kaspchak, E., Queiroz, M. B., Almeida, M. M., Quast, E. and Quast, L. B. 2015. Influence of temperature and homogenisation on honey crystallisation. *Brazilian Journal of Food Technology* 18(2): 155-161.
- Dettori, A., Tappi, S., Piana, L., Dalla Rosa, M. and Rocculi, P. 2018. Kinetic of induced honey crystallisation and related evolution of structural and physical properties. *LWT - Food Science and Technology* 95: 333-338.
- Hempattarasuwan, P., Settachaimongkon, S. and Duangmal, K. 2019. Impact of botanical source and processing conditions on physicochemical properties and antioxidant activity of honey in the northern part of Thailand. *International Journal of Food Science and Technology* 54: 3185-3195.
- Jaturonglumlert, S. and Kiatsiriroat, T. 2010. Heat and mass transfer in combined convective and far-infrared drying of fruit leather. *Journal of Food Engineering* 100: 254-260.
- Karasu, S., Toker, O. S., Yilmaz, M. T., Karaman, S. and Dertli, E. 2015. Thermal loop test to determine structural changes and thermal stability of creamed honey: rheological characterisation. *Journal of Food Engineering* 150: 90-98.
- Lupano, C. E. 1997. DSC study of honey granulation stored at various temperatures. *Food Research International* 30(9): 683-688.
- Mora-Escobedo, R., Moguel-Ordóñez, Y., Jaramillo-Flores, M. E. and Gutiérrez-López, G. F. 2006. The composition, rheological and thermal properties of Tajonal (*Viguiera dentata*) Mexican honey. *International Journal of Food Properties* 9(2): 299-316.
- Nurul Zaizuliana, R., Anis Mastura, A., Abd Jamil, Z., Norshazila, S. and Zarinah, Z. 2017. Effect of storage conditions on the crystallisation behaviour of selected Malaysian honeys. *International Food Research Journal* 24: S475-S480.
- Shinn, J. M. and Wang, S. L. 1990. Textural analysis of crystallized honey using response surface methodology. *Canadian Institute of Food Science and Technology Journal* 23(4-5): 178-182.
- Sobrino-Gregorio, L., Vargas, M., Chiralt, A. and Escriche, I. 2017. Thermal properties of honey as affected by the addition of sugar syrup. *Journal of Food Engineering* 213: 69-75.
- Suriwong, V., Jaturonglumlert, S., Varith, J., Narkprasom, K. and Nitatwichit, C. 2020. Crystallisation behaviour of sunflower and longan honey with glucose addition by absorbance measurement. *International Food Research Journal* 27(4): 727-734.
- Tomaszewska-Gras, J., Bakier, S., Goderska, K. and Mansfeld, K. 2015. Differential scanning calorimetry for determining the thermodynamic properties of selected honeys. *Journal of Apicultural Science* 59(1): 109-118.
- Venir, E., Spaziani, M. and Maltini, E. 2010. Crystallization in "Tarassaco" Italian honey studied by DSC. *Food Chemistry* 122(2): 410-415.
- Zamora, M. C. and Chirife, J. 2006. Determination of water activity change due to crystallisation in honeys from Argentina. *Food Control* 17(1): 59-64.
- Zheng, Q., Zhang, Y., Montazerian, M., Gulbiten, O., Mauro, J. C., Zanutto, E. D. and Yue, Y. 2019. Understanding glass through differential scanning calorimetry. *Chemical Reviews* 119(13): 7848-7939.