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Glass Transition Temperature of Honey Using Modulated Differential Scanning Calorimetry (MDSC): Effect of Moisture Content

－ Research Note －

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Abstract

Glass transition phenomena in nine Korean pure honeys (moisture content 18.3～20.1%) and honey-water mixtures by different water contents (0, 2, 5, and 10% w/w) were investigated with modulated different scanning calorimetry (MDSC). The total, reversing, and non-reversing heat flows were quantified during heating using MDSC. Glass transition was observed from reversing heat flow separated from the total heat flow. The glass transition temperatures (T_g) of pure honeys, which are in the range of -42.7°C to -50.0°C, varied a lot with low determination coefficient (R^2=0.63), whereas those of honey-water mixtures decreased with a decrease in honey content. The T_g values were also more significantly different among honey-water mixtures when compared to pure honeys, indicating that in the honey-water mixture system the T_g values appear to be greatly dependent on moisture content. The measured heat capacity change (ΔC_p) was not influenced by moisture content.

Key words: honey, moisture content, different scanning calorimetery, glass transition temperature

INTRODUCTION

Honey is the viscous and sweet substance produced by the honeybee from the nectar of plants (1). Honey, either in its pure state or mixed with water, is used as an ingredient in the food industry for its sweetness, texture, and preservative properties (2). Physical properties of honey depend mainly on its composition (sugars and moisture content). The moisture content is an important quality factor which influences the storability of honey. Therefore, knowledge of the physical properties of honey is required to best estimate the extent to which changes in quality will occur. In particular, it is known that thermal transition of honey from a glassy to a rubbery-like state is one of its important physical properties. To understand the effects of moisture content on the thermal transition of honey, several researchers have studied its glass transition (3-5).

Glass transition is a physical parameter that refers to the change in the physical state of amorphous materials between the glassy and rubbery states at a temperature called the glass transition temperature (T_g) (6). In food systems, the T_g has a major role in influencing the food's stability because water in the concentrated serum phase does not participate in any reactions due to its decreased molecular free volume and mobility (3). It has been known that water works as a strong plasticizer in food systems, such that an increasing amount of water decreases the T_g. In the honey industry, it is also recognized that the water content of a honey is an important quality factor because water levels determine the possibility of spoilage by fermentation (7). Because of the importance of moisture content in the keeping quality or storability of honey, the T_g, which is highly sensitive to the moisture content, has been studied by some researchers (3-5). They found that the T_g is greatly related to moisture content. The most common technique used to determine T_g of foods is the differential scanning calorimetry (DSC), which detects the change in heat capacity. Recently however, modulated DSC (MDSC) is being used to increase the sensitivity and resolution of complex thermal events.

In an MDSC experiment, a sinusoidally-varying temperature program is used instead of the conventional linear heating or cooling ramp (8). This newer type of temperature program provides the benefits of separating reversible and non-reversible thermal events, improving resolution of closely occurring or overlapping transitions and results in greater precision in the measurement of heat capacity. The total, reversible, and non-reversible heat flows can be quantified during the transition of the samples in one single scan. In most of studies regarding foods, MDSC analysis is used to characterize the glass transition, which is associated with reversible signals, and which could be differentiated from irreversible signals, such as the endothermic relaxation of amorphous materials, gelatinization, recrystallization, and protein denaturation. However, the applicability of MDSC for

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determining T_g of honeys has not been reported except for the study of Cordella et al. (9) who investigated the thermal behavior of authentic honeys and sugar syrups. In particular, no study has yet been published examining the effect of moisture content on the T_g of honeys using MDSC. Therefore, the main objectives of the present study were to determine the T_g of Acacia pure honeys and honey-water mixtures with different moisture contents using MDSC and to determine what effects, if any, moisture content had on their T_gs.

MATERIALS AND METHODS

Sample preparation

Nine Korean Acacia honeys (moisture content 18.3~20.1%) popular in Korea were purchased at a local supermarket. They were heated to 55°C for 1 hour in a water bath to dissolve crystals, and then kept in a 30°C room for 48 hr to remove air bubbles from the preheated honey samples, as described by Yoo (10). Honey-water mixture samples with a wide range of moisture content (0~10%) were also prepared by adding distilled water (0, 2, 5, and 10% w/w water content) to a pure honey.

Modulated differential scanning calorimetry (MDSC)

The phase transitions in honey samples were detected by a differential scanning calorimeter with modulation (TA Q200 Modulated DSC, TA Instruments Inc., New Castle, DE, USA) with a refrigerated cooling system (RCS). The instrument was calibrated with sapphire and indium. Nitrogen was used as purge gas at a flow rate of 50 mL/min. Samples (5 mg) were weighed directly onto aluminum DSC pans and hermitically sealed. Samples were also cooled to -80°C and then heated to 50°C at 3°C/min with modulation amplitude of ±0.477°C and period of 60 sec. Reversible and non-reversible heat flow signals were separated from the total heat flow signals (Fig. 1), and the T_g was determined from the reversing heat flow signal. The separation of these two thermal effects makes it possible to obtain higher reproducibility in the determination of the T_g. TA Universal Analyser^{TM} software was used to obtain the T_g and the change in heat capacity (ΔC_p). The mid-point T_g defined by the ASTM standard (E-1356-08) (11) was considered in this study, even though the onset and end-point T_g were also reported. The reported results are an average of the two or three measurements.

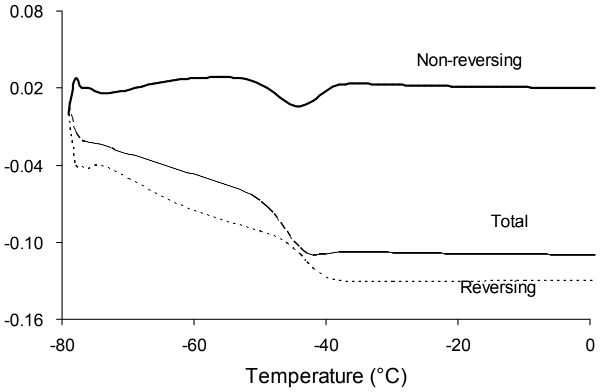

Fig. 1. Modulated differential scanning calorimetry thermograms of a honey sample (A3).

Statistical analysis

All results are expressed as mean±standard deviation. Analysis of variance (ANOVA) was performed using Statistical Analysis System software (version 9.1, SAS Institute, Cary, NC, USA). Differences in means were determined using Duncan's multiple-range test.

RESULTS AND DISCUSSION

The glass transition temperatures for honeys were determined from reversible heat flow curves obtained from MDSC. Glass transition temperatures (T_g) at three locations (onset, mid-point, and end point) of pure honey samples were determined from thermograms and summarized in Table 1. The T_g reported in this study is the mid-point temperature. As shown in Table 1, the T_g values of nine honey samples (A1~A9) varied between -42.7 and -50.0°C for a moisture content range of 18.3~

Table 1. Glass transition temperatures and heat capacity change (ΔC_p) of Korean acacia honey samples[1)]

Sample	Moisture content (%)	Glass transition temperature (°C)			ΔC_p (J/g/°C)
		Onset	Mid-point	End-point	
A1	20.1	-50.8±0.59	-50.0±0.17	-46.3±0.35	0.60±0.02
A2	18.3	-45.2±0.37	-42.7±0.30	-39.8±0.74	0.60±0.05
A3	18.9	-46.7±0.04	-44.5±0.21	-40.5±0.06	0.65±0.01
A4	19.9	-49.8±0.32	-47.4±0.15	-44.0±0.12	0.66±0.03
A5	19.0	-47.3±0.28	-45.6±0.52	-42.0±0.92	0.60±0.05
A6	19.3	-47.3±0.15	-45.1±0.84	-42.2±0.64	0.56±0.01
A7	19.6	-46.9±0.59	-44.6±0.37	-41.2±0.52	0.62±0.01
A8	19.2	-44.4±0.42	-43.1±0.62	-40.7±0.64	0.52±0.06
A9	19.4	-44.8±0.62	-43.8±0.42	-41.1±0.32	0.54±0.01

[1)] Values are mean±SD.

Table 2. Glass transition temperatures and heat capacity change (ΔC_p) of honey-water mixtures with different water contents (0, 2, 5, and 10% w/w)

Sample	Glass transition temperature (°C)			ΔC_p (J/g/°C)
	Onset	Mid-point	End-point	
Pure honey (0%)	-46.7 ± 0.04^a	-44.5 ± 0.21^a	-40.5 ± 0.06^a	0.65 ± 0.01^c
Honey+2% water	-52.4 ± 0.08^b	-49.8 ± 0.33^b	-47.5 ± 0.93^b	0.63 ± 0.01^c
Honey+5% water	-55.9 ± 0.59^c	-52.8 ± 0.98^c	-48.9 ± 0.27^b	0.73 ± 0.01^a
Honey+10% water	-68.4 ± 0.67^d	-63.8 ± 0.78^d	-60.5 ± 1.48^c	0.69 ± 0.01^b

$^{a\text{-}d}$Mean±SD values in the same column with different letters are significantly different ($p<0.05$).

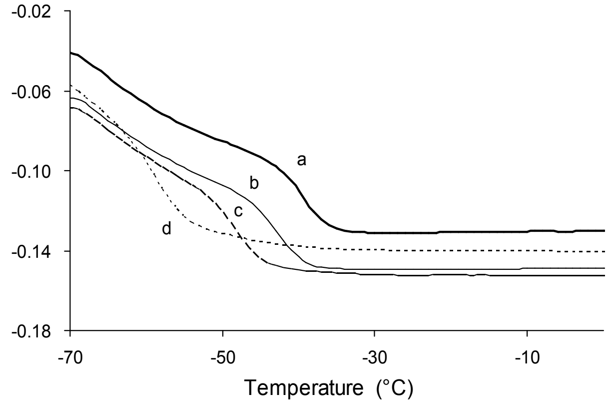

Fig. 2. Reversing heat flow thermogram of honey-water mixtures: a, pure honey; b, honey+2% water; c, honey+5% water; d, honey+10% water.

20.1%. The A1 with higher moisture content (20.1%) and A2 with lower moisture content (18.3%) exhibited the lower T_g (-50.0°C) and higher T_g (-43.1°C), respectively. The T_g values, in general, decreased with increasing moisture content. It is well known that the T_g in the food system is influenced by the moisture content due to the plasticization effect of water. Matveev et al. (12) reported that honeys with high moisture content exhibited low glass transition temperatures because of the plasticization effect of water molecules, which weakens hydrogen bonds as well as dipole-dipole and intra- and inter-macromolecular interactions. However, our results showed a poor linear relationship (R^2=0.63) with moisture content, even though the T_g values generally decreased with increasing moisture content, as described previously. This indicates that the differences in the composition of sugars in honey could also contribute the changes in T_g. Slade and Levine (13) reported that the T_g is a function of both moisture content and the type of solute. Ahmed et al. (4) also reported that floral source and environmental condition govern the T_g of honey. Therefore, the T_g of honey appears to be influenced by its composition and variety.

To investigate the effect of only moisture content on thermal transition, honey-water mixtures diluted from a pure honey sample (A3) were prepared and their T_gs were measured by MDSC, as described previously. The A3 sample was selected because it showed good reproducibility of T_g and ΔC_p measurements. As shown in Fig. 2, the MDSC reversible heat flow thermograms of honey-water mixtures with wide range of moisture content (0~10%) showed a clear shift in the baseline at its glass transition. The T_g values decreased significantly from -44.5 to -63.8°C with an increase in water content (Table 2), indicating that T_g values of honey-water mixtures with wide range of moisture content are influenced mainly by the moisture content. Similar observations have been reported by Kantor et al. (5) who measured the T_g of diluted honeys using conventional DSC. Lazaridou et al. (3) also reported that the plasticizing action of water is apparent in diluted honey samples, indicating that the T_g decreased significantly with increasing moisture content. As shown in Table 2, in particular, the addition of 2% water to honey resulted in a great shift of the T_g by 5.3~7.0°C. These results indicate that MDSC measurement is quite sensitive for detecting the effect of moisture content on T_g in the honey-water mixture system.

The heat capacity change (ΔC_p) values of pure honeys and honey-water mixtures are in the range of 0.52~0.66 J/g/°C and 0.63~0.73 J/g/°C, respectively (Table 1, 2). In general, it is known that the shift in ΔC_p is a measure of the fragility (or sensitivity) of amorphous materials to thermal changes and is influenced by moisture content, as described by Roos (6). He reported that strong liquids, which are not susceptible to thermal changes, show lower ΔC_p when compared to fragile liquids. In addition, it has been found that an increasing of moisture content decreases the T_g, but also increases the ΔC_p of the transition (14). However, there was no particular trend of the measured ΔC_p of either pure honeys or honey-water mixtures as a function of moisture content, indicating that the ΔC_p of honey was not influenced by moisture content (Table 1, 2). A similar trend was also observed for Australian honeys with different moisture contents (14.9~18.0%) (15).

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