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Dynamic Rheological Properties of Honey with Invert Sugar by Small-Amplitude Oscillatory Measurements

Hye-Mi Choi, Kyoung-Mo Kang, and Byoungseung Yoo*

Department of Food Science and Technology, Dongguk University, Seoul 100-715, Korea

Abstract Dynamic rheological properties of honeys with invert sugar at different mixing ratios of honey and invert sugar (10/0, 8/2, and 6/4 ratios) were evaluated at various low temperatures (-15, -10, -5, and 0°C) using a controlled stress rheometer for small-deformation oscillatory measurements. Honey-invert sugar mixtures displayed a liquid-like behavior, with loss modulus (G") predominating over storage modulus (G') (G">>G'), showing the high dependence on frequency (ω). The magnitudes of G' and G" increased with a decrease in temperature while their predominant increases were noticed at -10 and -15°C. The greater tan δ values were found at higher temperature and ratio of honey to invert sugar, indicating that the honey samples at subzero temperatures become more viscous with increased ratio of honey to invert sugar and temperature. The time-temperature superposition (TTS) principle was used to bring G" values at various temperatures together into a single master curve. The TTS principle was suitable for the honey samples in the liquid-like state. The progress of viscous property (G") was also described well by the Arrhenius equation with high determination coefficients (R^2=0.99). Dynamic rheological properties of honey samples seem to be greatly influenced by the addition of invert sugar.

Keywords: honey, rheology, dynamic modulus, invert sugar, time-temperature superposition, Arrhenius model

Introduction

Honey is a sweet, viscous substance elaborated by the honeybee from the nectar of plants (1). Rheological properties of honey, like other fluid foods, is important with respect to practical applications related to handling, storage, processing, and transport in industry (2). In general, changes in rheological characteristics of honey depend on moisture content, sugar composition, temperature, and the amount and size of crystals (3). The effect of temperature on rheological properties of honey needs to be studied because they are greatly influenced by a wide range of temperatures occurred during processing and storage. In general, dynamic rheometry for small-deformation oscillatory measurement provides valuable information on the viscoelastic properties of honeys without breaking their structural elements at various temperatures (4). In particular, it has been known that the low temperature may affect the changes in dynamic rheological properties of honey due to its crystallization, depending on the sugar composition and moisture content of the honey, as described by Sopade *et al.* (5) who examined dynamic rheological properties of various Australian honeys at subzero temperatures in the range of -15 to 0°C for their relationship to liquid-solid transformation. Therefore, it can be theoretically possible to predict and control the quality of honeys due to different crystallization processes of honeys at low temperatures because dynamic rheological characteristics can be greatly influenced by the crystallization of sugars presented in honey. However, no attempt has yet been made to study the dynamic rheological properties of honeys mixed with invert sugar that is used extensively in the adulteration of honeys. Honey is frequently adulterated with relatively cheap high-fructose corn syrup (HFCS) and invert sugar (6, 7).

Honey is essentially a mixture of sugar and water. When other sugars are applied to honey, some changes on its rheological properties may occur (8). Therefore, it is necessary to understand the dynamic rheological properties of a mixture of honey and invert sugar that are important for detecting adulteration in honey samples. The present study was undertaken to investigate the effect of invert sugar on dynamic rheological properties of honey at various low temperatures and to validate the Williams-Landel-Ferry (WLF) model as a tool for predicting the temperature dependence of the dynamic moduli of these honey samples mixed with invert sugar at low temperatures.

Materials and Methods

Materials and sample preparation Liquid invert sugar sample was obtained from Suikers G. Lebbe N.V. (Oostkamp, Belgium). An Acacia honey (water content 19.0%), which is the same moisture content as the invert sugar, was selected among Korean honeys purchased at a local supermarket. The water contents of honey samples were obtained by measuring the refractive index at 20°C using a digital refractometer (DR-A1 Abbe refractometer; Atago Co., Tokyo, Japan). The water content was determined based on a table given by the AOAC in method 31.119 (9). The honey was mixed with different quantities of invert sugar. Honey-invert sugar mixture samples were prepared by mixing invert sugar to obtain 0, 20, and 40% (weight basis) invert sugar levels. Therefore, the mixing ratios of honey (H) and invert sugar (IS) were H/IS = 10/0, 8/2, and 6/4. The ratios were chosen to determine the dynamic rheological differences between honey samples mixed with invert sugar by small-amplitude oscillatory measurements.

*Corresponding author: Tel: 82-2-2260-3368; Fax: 82-2-2264-3368
E-mail: bsyoo@dongguk.edu
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The rheological properties can be influenced by the presence of crystals and air bubbles in honey. Therefore, in the present experiment the honey samples were heated to 55°C for 1 hr in a water bath until all sugar crystals were dissolved. The honey-invert sugar mixtures were then mixed with mild agitation provided by a magnetic stirrer, and kept in a 30°C room for 48 hr to remove air bubbles from the preheated honey samples, as described by Yoo (4).

Sugar composition Sugar analysis (fructose, glucose, and sucrose) was performed by high performance liquid chromatography (HPLC, Nanospace SI2; Shiseido Fine Chemicals, Tokyo, Japan) using a Asahipak-NH2P-50 250×4.6 mm column with 0.8 mL/min flow rate. The mobile phase was acetonitrile and water (70:30). One g of honey was dissolved in acetonitrile and water (50:50) and transferred into 50 mL flask. The sample was poured through a 0.45 μm membrane filter and collected in sample vials. Twenty μL at 35°C was used for the analysis. The refractive-index detector (RI104; Shodex, Tokyo, Japan) was used to monitor the column effluent. A standard solution containing 0.5%(w/v) each of fructose, glucose, and sucrose was used to identify and quantify the individual sugar components in the honey samples.

Dynamic rheological measurements Dynamic rheological properties of honey samples were obtained with a TA AR1000 rheometer (TA Instruments Inc., New Cattle, DE, USA) at various low temperatures (-15, -10, -5, and 0°C), using a parallel plate system (4 cm diam.) at a gap of 500 μm. Dynamic rheological data were determined from frequency sweeps over the range of 0.63-48.3 rad/sec at 3% strain. The 3% strain was in the linear viscoelastic region. TA rheometer Data Analysis software (version VI. 1.76) was used to calculate storage (or elastic) modulus (G'), loss (or viscous) modulus (G"), and complex viscosity (η*), and to obtain the horizontal shift factors (a_T) for the time-temperature superposition (TTS) of the experimental data. Each measurement was taken after a 2-min rest following loading that allowed for temperature equilibrium to the required temperature. The G" values of honeys at -10 and -15°C were measured only in the frequency range of 0.62-8.90 rad/sec because their high values lie beyond the limits of the TA AR1000 rheometer used in this study. The dynamic rheological measurements were conducted in duplicate when there was good reproducibility and in triplicate when the discrepancy was >10% between the first 2 replicates. Results reported were an average of the 2 or 3 measurements.

Results and Discussion

Sugar composition It is well known that sugars represent the largest portion of honey composition (i.e., more than 95% of the honey solids). Honey consists mostly of fructose and glucose with trace amounts of disaccharides (sucrose and maltose). Sugars in honey are responsible for properties such as viscosity, hygroscopy, granulation, and energy value (11). The ratio of fructose to glucose depends largely on the nectar of plants and the average ratio of fructose to glucose is 1.2/1.0 (1). As shown in Table 1, all

Table 1. Sugar composition of honey (H)-invert sugar (IS) mixtures at different ratios of honey to invert sugar

H/IS ratio	Glucose (%)	Fructose (%)	Sucrose (%)	F/G ratio[1)]
10/0 (honey)	31.4	48.4	5.74	1.54
8/2	34.4	47.3	4.55	1.37
6/4	37.3	46.2	3.42	1.24
0/10 (invert sugar)	46.0	42.9	n.d.[2)]	0.93

[1)]F/G ratio: fructose/glucose ratio.
[2)]Not detected.

the samples except for pure invert sugar contained more fructose than glucose, indicating that the ratios of fructose to glucose are in the range of 1.24-1.54. The fructose content (48.4%) of pure honey decreased gradually with increasing honey to invert sugar ratio while the glucose content (31.4%) of pure honey increased. Moreover, the fructose/glucose ratio decreased with an increase in the content of invert sugar.

Dynamic rheological properties Figure 1 shows the changes in storage modulus (G'), loss modulus (G"), and complex viscosity (η*) as a function of the frequency (ω) for a representative honey at 0°C and the ratio of 8/2 (honey/invert sugar). The magnitudes of G' and G" steadily increased with an increase in ω, and the magnitudes of G" were much greater than those of G' at all values of ω, showing a high frequency dependency. However, the magnitudes of η* were independent of ω, giving a Newtonian plateau. Such behavior is typical of liquid-like solutions. The dynamic rheological data of log (G', G") versus log ω (rad/sec) for honeys with 3 different ratios of honey to invert sugar (10/0, 8/2, and 6/4) at 4 different temperatures (-15, -10, -5, and 0°C) were subjected to linear regression; the magnitudes of slopes and intercepts are summarized in Table 2. The magnitudes of G' and G" increased with a decrease in temperature. This is in agreement with the results of Yoo (4) who found

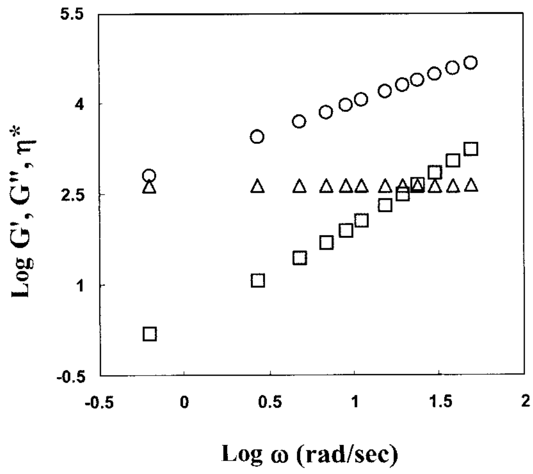

Fig. 1. Plot of log G' (□), log G" (○), and log η* (△) versus log ω of a typical honey-invert sugar mixture (8/2 ratio) at 0°C.

that dynamic moduli (G' and G") values decreased exponentially with increasing temperature from 0 to 30°C of Korean honeys with different varieties. Such increased dynamic moduli values at lower temperatures can be due to the increased crystallization (granulation) (12) and the free volume limitations near the glass transition at high concentrations of supersaturated sugar solutions (13, 14). They also decreased with increasing honey to invert sugar ratio, indicating that the viscoelastic properties decrease with a decrease in the ratio of fructose to glucose. Sopade *et al.* (5) also observed that increase in glucose content reduced the viscosity of honeys at subzero temperatures, while their viscosity increased with an increase in fructose content. Therefore, these results support the idea that the viscoelastic properties of pure honey can be decreased by the addition of invert sugar.

While there was a difference between slopes of G' for all honey samples, the slopes of G" except for honey samples (1.10 Pa·sec for 10/0 ratio; 1.20 Pa·sec for 8/2 ratio) at -15°C were almost the same, as shown in Table 2. The slopes (1.32-1.91 Pa·sec) of G' for these samples were relatively much higher than those (1.00-1.20 Pa·sec) of G", indicating that honey at low temperatures is more viscous than elastic. These results confirm an earlier observation that the slopes (1.38-1.80 Pa·sec) of G' for Korean honey of different varieties at a low temperature (0°C) were much higher than those (1.00-1.01 Pa·sec) of G" (4). Therefore, the rheological behavior of honey-invert sugar mixtures at subzero temperatures seems to be similar to that of a liquid-like macromolecular solutions. The tan δ (a ratio of G" to G') values were in the range of 7.93-213.7 (G">>G') and also increased with an increase in temperature and ratio of honey to invert sugar (Fig. 2). This indicates that the honey-invert sugar mixtures at subzero temperatures become much more viscous with increased temperature and ratio of honey to invert sugar.

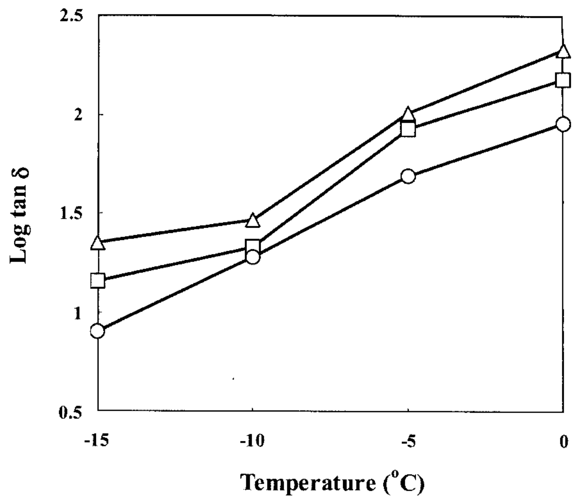

Fig. 2. Plot of log tan δ at 6.28 rad/sec versus temperature for honey-invert sugar mixtures at different ratios of honey to invert sugar. ○, 10/0; □, 8/2; △, 6/4.

Time-temperature superposition (TTS) From above dynamic rheological data, G' appears to be less important than G" due to its low value with respect to G" (G">>G'). Therefore, in this study the principle of TTS of honey-invert sugar mixtures at subzero temperatures is applied to investigate the temperature dependency of only G" values. In general, the rehological properties of fluid foods are strongly affected by temperature. It is a well-known phenomenon that increasing temperature would decrease the viscosity of fluid foods due to an increase in kinetic energy. Figure 3 shows the changes in G" values of honey-invert sugar mixtures at different low temperatures (-15-0°C). The magnitudes of G" decreased with an increase in temperatures. The dependence on temperature of G" appeared to follow the usual expectation of decreasing G" with increase in temperature with a high dependency on

Table 2. Slopes and intercepts (Pa·sec) of log (G′, G″) versus log ω (frequency, rad/sec) data of honey (H)-invert sugar (IS) mixtures at different temperatures and ratios of honey to invert sugar

H/IS ratio	Temperature (°C)	G′ Slope	G′ Intercept	G′ R^2	G″ Slope	G″ Intercept	G″ R^2
10/0	-15	1.81	665	1.00	1.10	19448	1.00
	-10	1.82	142	1.00	1.01	11860	1.00
	-5	1.91	14.3	1.00	1.01	3628	1.00
	0	1.89	4.37	1.00	1.02	1947	1.00
8/2	-15	1.85	180	0.99	1.20	8438	1.00
	-10	1.82	104	1.00	1.00	9919	1.00
	-5	1.90	4.97	1.00	1.02	2093	1.00
	0	1.79	1.59	1.00	1.00	1021	1.00
6/4	-15	1.32	92.9	1.00	1.00	3715	1.00
	-10	1.85	53.7	1.00	1.01	7349	1.00
	-5	1.86	3.94	1.00	1.00	1928	1.00
	0	1.73	0.75	1.00	1.00	613	1.00

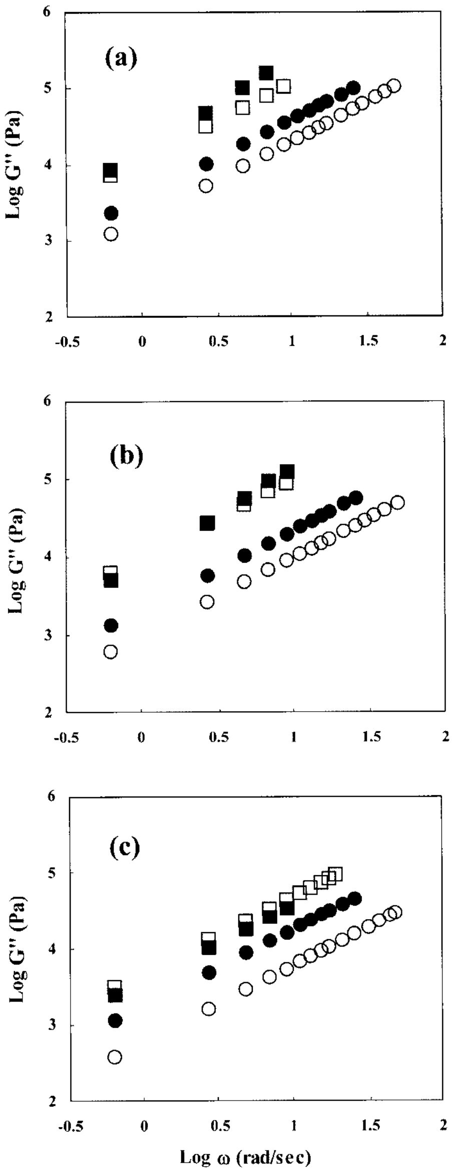

Fig. 3. Loss modulus (G") as a function of frequency (ω) for honey-invert sugar mixtures at different ratios of honey to invert sugar and various temperatures. ■ , -15°C; □ , -10°C; ● , -5°C; ○ , 0°C. (a) 10/0, (b) 8/2, and (c) 6/4.

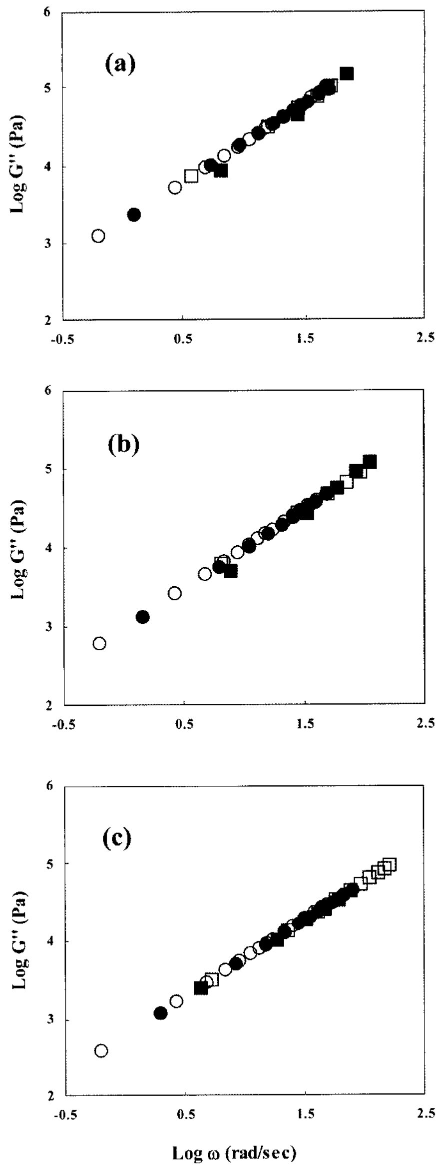

Fig. 4. Master curves of G" as a function of ω for honey-invert sugar mixtures at different ratios of honey to invert sugar and various temperatures. ■ , -15°C; □ , -10°C; ● , -5°C; ○ , 0°C. (a) 10/0, (b) 8/2, and (c) 6/4.

frequency (ω). In general, most of food materials, because of their viscoelastic nature, exhibit rheological behavior which is both temperature and time (frequency) dependent during deformation and flow. Therefore, from the knowledge that the time scale (or frequency) of the application of stress has a similar influence on mechanical properties, i.e., short time (high frequency) corresponds to low temperature and long time (low frequency) corresponds to high temperature, the principle of TTS is introduced (15). It is known that the TTS principle laterally shifts isothermal oscillatory frequency data using a shift factor to form a single master curve (16). The amount of shifting along the horizontal (x-axis) in a typical TTS plot required to align the individual experimental data into the master curve can be generally described using the WLF equation (Eq. 1) (17). At temperatures above the reference temperature, it takes less time to reach a particular response (the material responds faster, i.e., has a shorter relaxation time), so a_T is less than unity, and vice versa. The logarithm of the experimentally determined temperature shift factor is usually plotted as a function of temperature.

$$\text{Log } a_T = \frac{-C_1(T-T_o)}{C_2+(T-T_o)} \qquad (1)$$

where C_1 and C_2 are the temperature dependent constants, T_o is the reference temperature (K), T is the measurement temperature (K) and a_T is the shift factor. In this study the values of horizontal a_T for TTS of the data were calculated

Table 3. Activation energies (Ea) of honey (H)-invert sugar (IS) mixtures at different ratios of honey to invert sugar

H/IS ratio	Ea (kJ/mol)	R^2
10/0	94.5	0.99
8/2	109.9	0.99
6/4	93.8	0.99

using the TA Rheometer TTS Software. A master curve of G" was created by shifting the initial G" curves to a reference G" curve at a temperature of 273K (0°C) using the WLF equation (Fig. 4). The G" values measured at other temperatures (-15, -10, and -5°C) were moved to the reference G" curve using a_T to reduce the w values into a single master curve. In this way, it was found that G" values of honey samples could be superposed into a master curve using a reduced frequency. This indicates that the TTS allowed the estimation of dynamic rheological properties of honey-invert sugar mixtures over the frequency range which is otherwise inaccessible to the range of experimental measurement.

The effect of temperature on shift factor (a_T) can also be described by the Arrhenius equation (Eq. 2).

$$\text{Log } a_T = (Ea/2.303R)(1/T - 1/T_o) \quad (2)$$

where Ea is activation energy (kJ/mol), R is the gas constant (8.3144 J/mol·K), and T_o is the reference temperature. Activation energy values were determined from the slope obtained by plotting the logarithm of a_T versus the inversed temperature difference ($1/T - 1/T_o$). The Ea values were determined to be in the range of 93.8-109.9 kJ/mol with high determination coefficients (R^2= 0.99) (Table 2), showing that the dependence of a_T for honey samples on subzero temperatures followed the Arrhenius equation. Ea value (109.9 kJ/mol) at 8/2 ratio was much higher than those at 10/0 (94.5 kJ/mol) and 6/4 ratios (93.8 kJ/mol), indicating that a higher Ea means increased sensitivity of rheological material functions to temperature. This may indicate that the sample with lower ratio of honey to invert sugar (8/2 ratio) behaves more viscoelastic. This was supported by more pronounced dynamic moduli at 8/2 ratio than those at 6/4 ratio, as shown in Table 1 and Fig. 2.

In the light of dynamic rheological data presented in this study, it can be concluded that dynamic rheometry for small-deformation oscillatory measurements appears to be a useful method for detecting the effect of adulteration on structural properties of honey. However, the dynamic moduli of honey-invert sugar mixtures could be affected by other factors, such as honey variety, crystallization, and other polymeric compounds presented in the honey. Therefore, more research is required to determine the effect of these factors on the dynamic rheological properties in the honey-invert sugar systems.

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