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Dynamic Rheological Properties of Honeys at Low Temperatures as Affected by Moisture Content and Temperature

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Abstract Dynamic rheological properties of honey samples with 3 different moisture contents (17.2, 19.0, and 21.0%) were evaluated at various low temperatures (−15, −10, −5, and 0°C) using a controlled stress rheometer. The honey samples 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" decreased with an increase in temperature and water content while a predominant increase of G' was noticed at −15°C. The time-temperature superposition (TTS) principle was applied to bring G" values for honeys at various temperatures together into a master curve. The G" over the temperature range of −15 to 0°C obeyed the Arrhenius relationship with a high determination coefficient (R^2=0.98-0.99). Activation energy value (Ea=112.4 kJ/mol) of honey with a moisture content of 17.2% was higher than those (Ea=98.8-101.1 kJ/mol) of other honey samples with higher moisture contents.

Keywords: honey, rheology, activation energy, time-temperature superposition (TTS)

Introduction

Honey is the viscous and sweet substance elaborated by the honeybee from the nectar of plants (1). Viscosity of honey is one of its important physical properties and correlates significantly with its other physicochemical and sensory properties (2). In particular, the viscosity in processing and handling of honeys influences the rate of extraction of honey from the combs, the rate of straining, the mixing of different honey types, spreading property, pumping, and packaging (3). Therefore, studies on rheological properties of honeys, like other fluid foods, could be important for applications related to proper handling, shelf-life, processing, quality control, and sensory analysis.

It has been known that the structural and rheological characteristics of honey depend on moisture content, temperature, and the amount and size of crystals. They are also influenced by the composition of individual sugars, and the amount and type of colloids present in honey (4). In particular, knowledge of the effect of temperature on rheological properties of honey is necessary for its production, processing, and storage. Therefore, many researchers have studied the rheological properties of honey as a function of temperature at a specific moisture content (5-9). However, little information is available on the effect of temperature on dynamic rheological properties of honeys with different moisture contents except for the study of Yoo (8) who studied dynamic rheological properties of various Korean honeys at different temperatures above 0°C. In general, it can be expected that the low temperature may also affect the changes in dynamic rheological properties of honey due to its crystallization, depending on the sugar composition and moisture content of the honey. Assuming that dynamic rheological properties of honeys are greatly influenced by low temperatures, it is theoretically possible to predict and control the quality of honeys due to their different crystallization processes. However, there is still little comprehensive information available on the effect of moisture content on dynamic rheological behavior of honeys at different low temperatures (below 0°C). Therefore, the main objective of the present study was to determine the dynamic rheological properties of honey samples at low temperatures as a function of moisture content and temperature.

Materials and Methods

Sample preparation Poly-flower honey (17.2% water content) popular in Korea was purchased at a local supermarket. Diluted honey samples with higher water contents were prepared by adjusting with distilled water to 2 different water contents (19.0 and 21.0%). 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 (10).

The presence of crystals and air bubbles can influence the rheological properties (6). Therefore, in the present experiment the honey samples were heated to 55°C for 1 hr in a water bath to dissolve the crystals, and then kept in a 30°C room for 48 hr to remove air bubbles from the preheated 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 diameter) at a gap of 500 μm. Dynamic rheological data were determined from frequency sweeps over the range of 0.63-62.8 rad/sec at 3% strain. The 3% strain was in the linear viscoelastic

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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" of honey at −15°C and 17.2% moisture content was measured only in the frequency range of 0.63-8.90 rad/sec because its high value lies beyond the limits of the TA AR1000 rheometer used in this study. The rheological measure-ments in dynamic shear were conducted in duplicate. Results reported were an average of the 2 measurements.

Results and Discussion

Dynamic rheological behaviors Figure 1 shows storage modulus (G'), loss modulus (G"), and complex viscosity (η*) as a function of the frequency (ω) for a representative honey at −5°C and 19.0% moisture content. While the magnitudes of G' and G" increased with an increase in ω showing a high frequency dependency, the magnitudes of η* were independent of ω. This tendency is in good

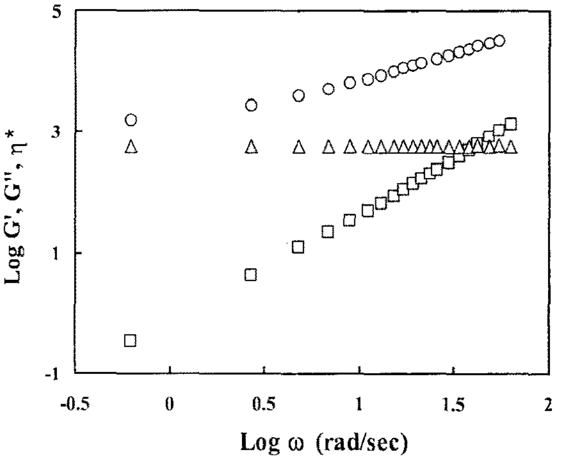

Fig. 1. Plot of log G' (□), log G" (O), and log η* (△) vs. log ω of a honey sample at 19.0% moisture content and −5°C.

agreement with those found for other honey samples (8,11,12). The dynamic rheological data of log (G', G") vs. log ω (rad/sec) for honeys with three different moisture contents (17.2, 19.0, and 21.0%) at 4 different temperatures (−15, −10, −5, and 0°C) were subjected to linear regression and Table 1 contains the magnitudes of slopes, intercepts, and R^2. The G' and G" values increased with decrease in temperature and moisture content, and the values of G" were much higher than those of G'. This is in agreement with the results of Lazaridou *et al.* (12) who found that G" values decreased exponentially with increasing moisture content of honey. Quintas *et al.* (13) also reported that the viscosity of supersaturated sucrose solutions in the concentration range of 70-85%(w/w) increased with increase in concentration and with decrease in temperature. Such increased dynamic moduli (G' and G") values at lower temperatures and moisture contents can be attributed to the increased crystallization (granulation) and the lower molecular immobility of honey, as described by Bhandari *et al.* (14). They may also be due to the free volume limitations near the glass transition at high concentrations of supersaturated sugar solutions, as noted by Al-Malah *et al.* (5) and Quintas *et al.* (13). However, the G' and G" values of honeys could also be affected by other factors, such as sugars and other polymeric compounds presented in the honey (4, 14). These factors were not considered in examining the dynamic rheological properties of honeys in this study. More research is needed to understand the effect of these factors other than temperature and moisture content on the dynamic rheological properties of honeys.

While there was noticeable changes in slopes of G' for all honey samples, the slopes of G" were the same (Table 1). The slopes (1.56-2.04 Pa·sec) of G' for all samples were relatively much higher than those (0.99-1.02 Pa·sec) of G", indicating that honey at low temperatures is more viscous than elastic. The same effect was observed earlier in other studies (4,11). Such dynamic rheological behavior seems to be similar to that of a liquid-like solutions or diluted solutions. In general, tan δ (a ratio of G" to G') is a clear indication of relative response of elastic and viscous parts of a sample, and its viscoelastic behavior can be evaluated. As shown in Fig. 2, the tan δ values at 6.28 rad/sec, which were in the rang of 19.8-504.4 (G">>G'), increased with

Table 1. Slopes and intercepts (Pa·sec) of log (G', G″) vs. log ω (frequency, rad/sec) data of honeys with differentmoisture contents at various temperatures

Moisture content	Temperature	G′			G″		
(%)	(°C)	Slope	Intercept	R^2	Slope	Intercept	R^2
17.2	-15	1.63	118	0.99	0.99	7575	0.99
	-10	1.79	25.4	0.99	1.00	3672	0.99
	-5	1.81	3.33	0.99	1.00	1533	0.99
	0	1.81	0.57	0.99	1.00	529	0.99
19.0	-15	1.75	23.6	0.99	1.02	2347	0.99
	-10	2.04	2.69	0.99	0.99	1249	0.99
	-5	1.95	0.65	0.99	1.00	565	0.99
	0	1.67	0.17	0.99	1.00	205	0.99
21.0	-15	1.79	1.82	0.99	1.01	755	0.99
	-10	1.76	0.53	0.99	1.01	374	0.99
	-5	1.61	0.15	0.99	1.00	165	0.99
	0	1.56	0.05	0.98	1.00	70.6	0.99

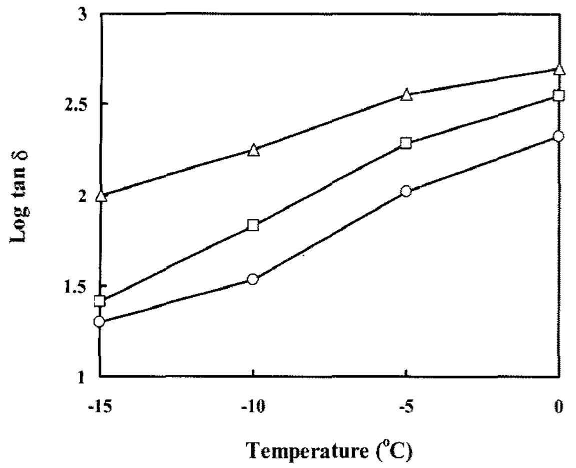

Fig. 2. Plot of log tan δ at 6.28 rad/sec vs. temperature for honey samples at different moisture contents. ○, 17.2%; □, 19.0 %; △, 21.0%.

increase in moisture content and temperature, indicating that the honey samples at low temperatures become much more viscous with increased moisture content and temperature. Therefore, in this study the effect of temperature on dynamic rheological pro-perties of honeys was characterized by G" values alone.

Time-temperature superposition (TTS) Figure 3 shows the changes in G" values of honey samples in the temperature range of −15 to 0°C. The magnitudes of G", which are related to the viscous response, decreased with increasing 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 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 (16). Recently, only a few researchers have used small deformation measurements to investigate the temperature dependence of the viscoelastic properties of food biopolymer solutions based on TTS principle (16,17). In the present study the TTS principle of honeys at various low temperatures was applied to investigate the temperature dependency of G". It is known that the TTS principle laterally shifts isothermal oscillatory frequency data using a shift factor to form a single master curve (17). The resulting response covers an expanded frequency range, which can be very useful for approximating the behavior of a material at frequencies or times inaccessible with the instrument used to obtain the original data, as indicated by Kao *et al.* (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) (18).

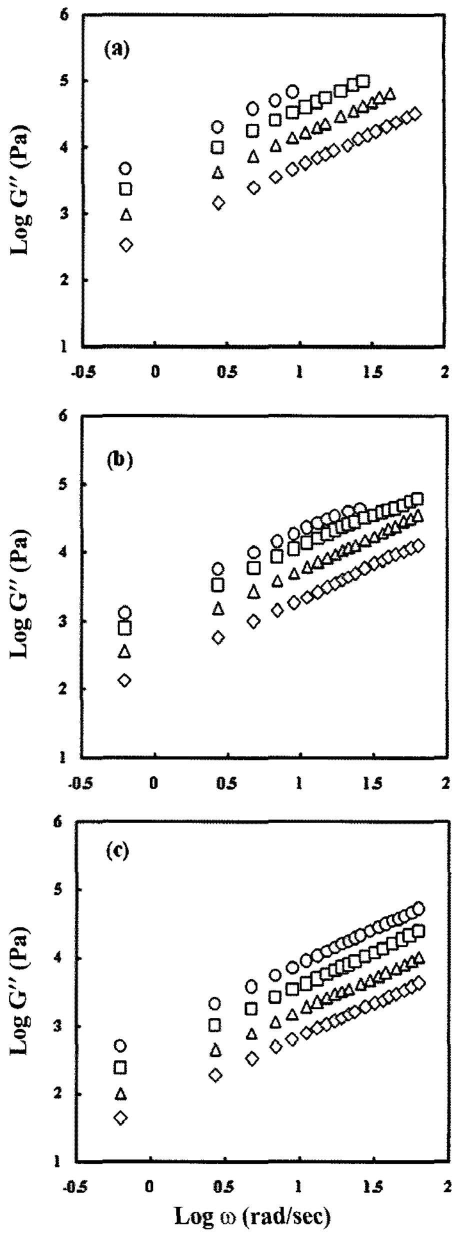

Fig. 3. Loss modulus (G") as a function of frequency (ω) for honey samples with different moisture contents at various temperatures. ○, −15°C; □, −10°C; △, -5°C; ◇, 0°C. (a) 17.2%, (b) 19.0%, and (c) 21.0%.

$$\log a_T = \frac{-C_1(T-T_o)}{C_2+(T-T_o)} \quad (1)$$

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 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 ω values into a master curve. In this way, it was found that G" values of

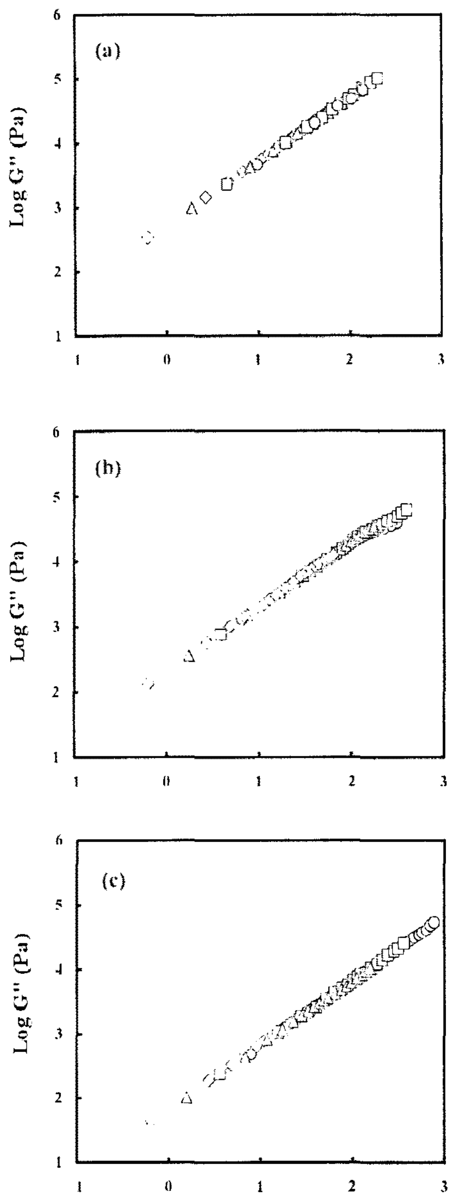

Fig. 4. Master curves of G'' as a function of ω for honey samples with different moisture contents at various temperatures. ○, −15 °C; □, −10°C; △, −5°C; ◇, 0°C. (a) 17.2%, (b) 19.0%, and (c) 21.0%.

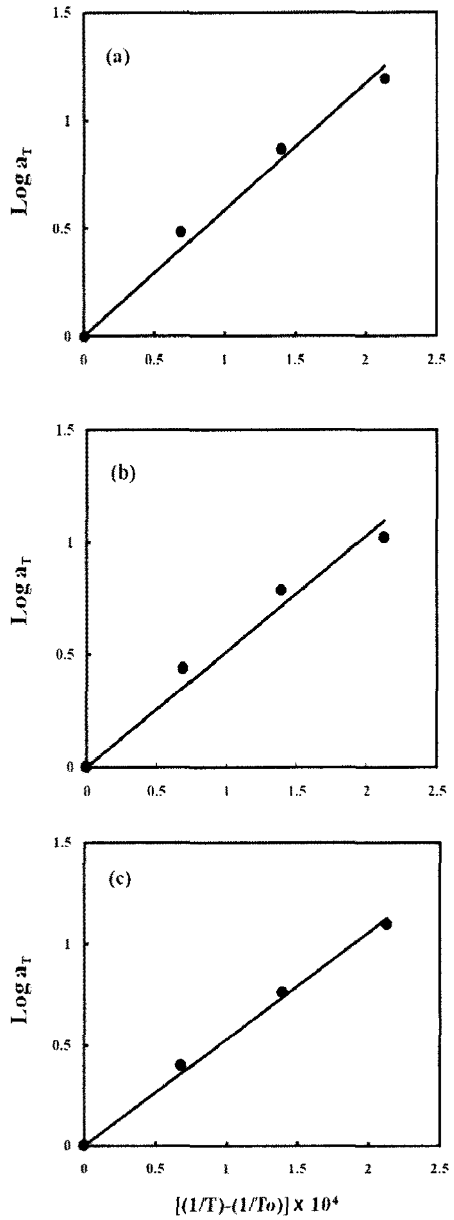

Fig. 5. Arrhenius fit of shift factors for G'' data of honeys with different moisture contents. (a) 17.2%, (b) 19.0%, and 21.0%.

honey samples could be superposed into a master curve using a reduced frequency, indicating that the TTS principle could also be used successfully for the honeys at various low temperatures. Therefore, it was found that the TTS approach is important for predicting and understanding changes in dynamic properties of honeys at low temperatures over time in response to change in temperature.

Temperature dependence of TTS shift factor As shown in Fig. 5, there is a linear variation of shift factor (a_T) with temperature, which can be described by the Arrhenius equation (Eq. 2).

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

where Ea is activation energy (kJ/mol), R is the gas constant (8.3144 J/mol · K), and T_o is the reference temperature. The Ea values were determined to be in the range of 98.8-112.4 kJ/mol with high determination coefficients (R^2=0.98-0.99) (Table 2), showing that the dependence of a_T for honeys on low temperatures followed the Arrhenius equation. Such high Ea values of honey samples mean that their rheological properties are more temperature-dependent in the moisture content range studied. Ea value (112.4 kJ/mol) at 17.2% moisture content was much higher than those at 19.0% (101.1 kJ/mol) and 21.0% (98.8 kJ/mol), indicating that the lower the moisture content, the higher the Ea values. This may suggest that at higher concentrations (lower moisture contents) there is a lower molecular mobility of honey, resulting in a deviation from the Arrhenius behavior. The same effect was observed earlier in gellan polysaccharide (19). Kasapis and Sworn (20) also reported that activation energy describes the energy associated with relaxation mechanism at cross-

Table 2. Activation energies (Ea) of honey samples with different moisture contents

Moisture content (%)	Ea (kJ/mol)	R^2
17.2	112.4	0.98
19.0	101.1	0.98
21.0	98.8	0.99

links or points of entanglement within material. Therefore, the higher Ea of honey at lower moisture content also means that a greater amount of energy is required for molecules rearrangement.

Acknowlegments

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References

1. White JW. Honey. Adv. Food Res. 24: 287-374 (1978)
2. Anupama D, Bhat KK, Sapna VK. Sensory and physico-chemical properties of commercial samples of honey. Food Res. Int. 36: 183-191 (2003)
3. Yanniotis S, Skaltsi S, Karaburnioti S. Effect of moisture content on the viscosity of honey at different temperatures. J. Food Eng. 72: 372-377 (2006)
4. Bhandari B, D'Arcy B, Chow S. Rheology of selected Australian honeys. J. Food Eng. 41: 65-68 (1999)
5. Al-Malah KIM, Abu-Jdayil B, Zaitoun S, AL-Majeed Ghzawi A. Application of WLF and Arrhenius kinetics to rheology of selected dark-colored honey. J. Food Process Eng. 24: 341-357 (2001)
6. Abu-Jdayil B, Al-Majeed Ghzawi A, Al-Malah KIM, Zaitoun SJ. Heat effect on rheology of light- and dark-colored honey. J. Food Eng. 51: 33-38 (2002)
7. Kim C, Chang YH, Yoo B. Flow behavior of Korean honey. Food Sci. Biotechnol. 12: 691-693 (2003)
8. Yoo B. Effect of temperature on dynamic rheology of Korean honeys. J. Food Eng. 65: 459-463 (2004)
9. Juszczak L, Fortuna T. Rheology of selected Polish honeys. Food Eng. 75: 43-49 (2006)
10. AOAC. Official Methods of Analysis of AOAC Intl. 14th ed. Association of Official Analytical Communities, Arlington, VA, USA (1984)
11. Choi HM, Kang KM, Yoo B. Dynamic rheological properties of honey with invert sugar by small-amplitude oscillatory measurements. Food Sci. Biotechnol. 16: 610-614 (2007)
12. Lazaridou A, Biliaderis CG, Bacandritsos N, Sabatini AG. Composition, thermal and rheological behaviour of selected Greek honeys. J. Food Eng. 64: 9-21 (2004)
13. Quintas M, Brandao TRS, Silva CLM, Cunh RL. Rheology of supersaturated sucrose solutions. J. Food Eng. 77: 844-852 (2006)
14. Bhandari B, D'Arcy B, Kelly C. Rheology and crystallization kinetics of honey: Present status. Int. J. Food Prop. 2: 217-226 (1999)
15. Mossel B, Bhandari B, D'Arcy B, Caffin N. Use of Arrhenius model to predict rheological behaviour in some Australian honeys. Lebensm. -Wiss. -Technol. 33: 545-552 (2005)
16. Kao N, Bhattacharya SN, Shanks R, Coopes IH. The effect of temperature on the viscoelastic properties of model and industrial dispersions. J. Rheol. 42: 493-506 (1998)
17. Nikerson MT, Paulson AT, Speers RA. A time-temperature rheological approach for examining food polymer gelation. Trends Food Sci. Tech. 15: 569-574 (2004)
18. Williams ML, Landel RF, Ferry JD. The temperature dependence of relaxation mechanisms in amorphous polymers and other glass-forming liquids. J. Am. Chem. Soc. 77: 3701-3706 (1955)
19. Nickerson MT, Paulson AT, Speers RA. Time-temperature studies of gellan polysaccharide gelation in the presence of low, intermediate, and high levels of co-solutes. Food Hydrocolloid 18: 1072-1079 (2004)
20. Kasapis S, Sworn G. Seperation of the variables of time and temperature in the mechanical properties of high sugar/polysaccharide mixtures. Biopoylmers 53: 40-45 (2000)