



Effect of Glass Transition Temperature Range on the Caking Behavior of Freeze-dried Carbohydrate Blend Powders

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Abstract

Glass transition temperature (T_g) and degree of caking for maltodextrin with added plasticizers (glucose, maltose, and sorbitol) were investigated. Onset and offset T_g s were evaluated by differential scanning calorimetry. From the onset and offset T_g -curves and water sorption isotherm, each critical water activity (a_{wc}) value was determined (water activity at each $T_g = 25$ °C). The a_{wc} range between onset T_g and offset T_g was extended by the addition of plasticizers. The degree of caking increased at a water activity just above a_{wc} of onset T_g , and completely caked at a water activity just below a_{wc} of offset T_g . Effect of a_w on the degree of caking became more gradual with the addition of plasticizers because of the extended a_{wc} range. According to the dependence of viscosity on temperature and water activity, a predictive model for the caking of amorphous powders was proposed based on the onset and offset T_g curves.

Keywords Glass transition temperature · Water sorption isotherm · Mechanical relaxation · Caking · Viscosity

Introduction

Amorphous food powders show glass-to-rubber transition (glass transition) upon changes in temperature and water content. Glass transition is characterized by the glass transition temperature (T_g) [1]. Glassy amorphous powders ($T < T_g$) have a solid-like property based on the extremely low molecular mobility and/or high viscosity [2]. Thus, physical stability is expected for the amorphous powder, and caking [3] and re-crystallization [4] are prevented. Rubbery amorphous powders ($T > T_g$), on the other hand, have a liquid-like property, and physical deteriorations may occur depending on the storage time. Since the T_g of amorphous food powders decreases with an increase in water content, glass transition is caused by water sorption

even at a constant temperature; when the T_g becomes lower than ambient temperature (typically 25 °C) as a result of water sorption, the glassy material changes to a rubbery material. The effect of water content on T_g has been described as the T_g curve. From the T_g curve, the water content at $T_g = 25$ °C can be determined as critical water content (w_c) [5]. In addition, w_c is converted to critical water activity (a_{wc}) through the effect of water activity (a_w) on the equilibrium water content of materials (water sorption isotherm). The values of w_c and a_{wc} help to characterize resistance to the physical deteriorations induced by water sorption [5, 6].

Caking is a physical phenomenon in which free-flowing powders are transformed into lumps, attributable to deformation and bridging of sticky particles as a result of plasticization and a decrease of surface viscosity [6, 7]. Caking requires relatively high molecular mobility and/or low viscosity to promote viscous flow; therefore, the T_g curve is useful to predict the caking of amorphous food powders [6–8]. Caking of amorphous food powders, however, does not always change drastically just at T_g . In our previous study [9], the caking behavior of maltodextrin (MD) and maca (*Lepidium meyenii* Walp.) powder was compared; the MD was a water-soluble carbohydrate polymer, and the maca powder was a mixture of protein (14.8%), fat (2%), and carbohydrate (69%). As expected, the degree of caking for MD powder was negligible below

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the a_{wc} (0.575) and increased drastically up to 100% above the a_{wc} . The degree of caking for maca powder, on the other hand, gradually increased from a slightly lower a_w than the a_{wc} (0.258), and the degree of caking drastically increased at higher a_w than 0.576. Two reasons why MD and maca powder showed completely different caking behavior were suggested. One reason is the dispersions (typically 23% starch and 23% water-insoluble fiber) that exist in maca powder [10]. When amorphous powder forms a fragile cake, the cake will be destroyed by sieving, and as a result the degree of caking cannot be determined. Since some dispersion contained in maca powder would have prevented the construction of a hard cake [8], there was no drastic increase in the degree of caking above a_{wc} . The other reason is the difference in the dependence of molecular mobility and/or viscosity on a_w in the rubbery state. Maca powder showed a continuously distributed glass transition behavior in the differential scanning calorimetry (DSC) thermogram. Taking into account the fact that glass transition occurs in a temperature range depending on the molecular mobility and/or viscosity change [11], it was suggested that the molecular mobility and/or viscosity required for caking was provided incrementally by the increase in a_w above a_{wc} . Similar caking behavior to maca powder has been reported in complex food powders such as fish protein hydrolysate [12], dairy-based infant formulas [13], skim milk [8, 14], spray-dried coffee [15], and spray-dried MD–lemon juice mixtures [16].

Glass transition occurs in a temperature range that is determined by the temperature dependence of molecular mobility and/or viscosity. That is, the temperature difference between the onset point of glass transition (T_g^{on}) and the offset point of glass transition (T_g^{off}) reflects the dependence of molecular mobility and/or viscosity on temperature [11, 17]. It is known that the T_g range of carbohydrate polymers becomes broader with the incorporation of carbohydrate-based plasticizers [18, 19]. In this study, thus, freeze-dried water-soluble maltodextrin (MD) and carbohydrate-based plasticizers including glucose, maltose, and sorbitol blend powders were employed as model food samples, and the effect of T_g range on caking behavior was investigated. Since there was no water-insoluble material (dispersions) in the model samples, it was expected that the effect of T_g range on the caking behavior of the amorphous food powder could be focused. In addition, the T_g range corresponded to the dependence of molecular mobility and/or viscosity on temperature and a_w , and a predictive model for the caking of water-soluble amorphous powders was proposed based on the dependence of viscosity on a_w . Caking is a deteriorative phenomenon in the powder food industry as it negatively affects food processing and handling. This study is expected to be a better predictive approach for the caking of amorphous food powders.

Material and Methods

Materials

Maltodextrin (MD) with a dextrose equivalent (DE) of 17–21 and glucose monohydrate were provided by San-ei Sucochemical Co., Ltd. (Aichi, Japan). Maltose monohydrate and sorbitol (D-glucitol) were purchased from Nacalai Tesque Inc. (Kyoto, Japan).

Sample Preparation

The MD and glucose were mixed at dry weight fractions of glucose = 0.1 and 0.2, maltose = 0.1, and sorbitol = 0.1. Samples are identified by the dry weight fraction and the initial character of the plasticizers hereafter. For example, MD:glucose = 0.8:0.2 and MD:maltose = 0.9:0.1 are referred to “G0.2” and “M0.1,” respectively. The mixtures and MD (non-additive sample) were dissolved in 35% (w/w) aqueous solutions by the addition of distilled water. The solution was distributed to an aluminum container and frozen in a freezer at -20 °C. The frozen samples were then transferred to a pre-cooled chamber and freeze-dried at approximately 11 Pa as the temperature was increased from -35 to 5 °C in a stepwise fashion over a 48-h period. The freeze-dried solids were powdered using a mixer.

Water Sorption Isotherm

Freeze-dried powder samples (0.5 g) were placed in an aluminum dish (40 mm diameter), and residual moisture of the samples was removed by vacuum-drying at 80 °C (stage temperature) for 6 h. The fully dried samples were equilibrated at 25 °C for longer than 7 days in a desiccator with saturated salts: LiCl ($a_w = 0.113$), CH_3COOK ($a_w = 0.225$), MgCl_2 ($a_w = 0.328$), K_2CO_3 ($a_w = 0.432$), $\text{Mg}(\text{NO}_3)_2$ ($a_w = 0.529$), NaBr ($a_w = 0.576$), KI ($a_w = 0.688$), and NaCl ($a_w = 0.753$). Equilibrium water content of the samples was determined gravimetrically by oven-drying at 105 °C for 16 h. Measurements were obtained in triplicate and the results averaged.

The water sorption isotherm behavior (equilibrium water content versus a_w) was analyzed using the Guggenheim, Anderson, and De Boer (GAB) equation:

$$W = \frac{W_m \cdot C \cdot K \cdot a_w}{(1 - K \cdot a_w) \cdot (1 + (C - 1) \cdot K \cdot a_w)} \quad (1)$$

where W is the equilibrium water content (g-water/g-solid), W_m is the amount of water strongly adsorbed to specific sites at the material surface (g-water/g-solid), and C and K are factors that correct the sorption properties of the monolayer with respect to the bulk liquid, and the properties of the

multilayer with respect to the bulk liquid, respectively [20]. The W_m , C , and K values were determined as fitting parameters using the KaleidaGraph software (version 3.6; Hulinks Inc., Tokyo, Japan).

Glass Transition Temperature

Glass transition temperature (T_g) of the samples was determined using a DSC (DSC 60, Shimadzu Instruments Inc., Tokyo, Japan). Alumina powder was used as a reference, and temperature and heat flow were calibrated with indium and distilled water, respectively. The sample (10–30 mg) was hermetically sealed into a DSC aluminum pan. The DSC measurement was carried out at 5 °C/min. To reset the thermal history of glassy samples, the DSC scan was repeated two times [21]. In the first scan, DSC measurement was stopped at a slightly higher temperature than the endothermic shift expected as glass transition, and then cooled down. In the second scan, DSC measurement was stopped at a much higher temperature than the T_g suggested by first scan. The DSC thermogram was analyzed using software interfaced with the DSC, and the T_g value was determined from the onset and offset points of the endothermic shift observed in the second scan. The measurements were performed in triplicate and the results averaged.

Isothermal Mechanical Relaxation

To confirm the validity of a_{wc} evaluated from the water sorption isotherm and T_g curve, isothermal mechanical relaxation measurements were carried out [9, 22]. The powder samples (20–30 mg) equilibrated at a_w conditions ($a_w = 0.113\text{--}0.753$) were placed in a stainless sample holder (diameter = 3 mm). The sample holder was placed on the heating stage (25 °C) of a texture meter (CR-150; Sun Scientific Co., Ltd., Tokyo, Japan) and compressed at 80 N (2.83 MPa) for 3 min with a plunger tightly fitted in the sample holder. The force-drop (ΔF) between the initial force (approximately 80 N) and the force after 3 min was evaluated as the degree of isothermal mechanical relaxation under a given condition. Measurements were obtained in triplicate and the results averaged.

Degree of Caking

The degree of caking was investigated as described previously [23] with minor modifications [9, 24]. Mixed powders were filtered through a 1.4-mm sieve with a vibration amplitude of 4.5 mm using a mechanical shaker (MVS-1; As One Instruments Co., Tokyo, Japan). Powder samples (approximately 0.5 g) were placed in an aluminum dish (diameter = 40 mm) and vacuum-dried at 80 °C for 6 h. The samples were equilibrated at 25 °C for 7 days in a desiccator with saturated salts as mentioned above. The equilibrated samples were

vacuum-dried at 25 °C for 6 h. The dried sample was weighed and then sieved under the same conditions as the first treatment. After weighing the amount of sample retained on the sieve, the degree of caking was evaluated as follows:

$$\text{Degree of caking (\%)} = 100 \times W_r/W_i \quad (2)$$

where W_r and W_i are the weight of retained and initial (pre-sieved) samples, respectively. The measurements were performed in triplicate and the results averaged.

Statistical Analysis

Analysis of variance (ANOVA) was performed using Tukey's HSD test ($p < 0.05$) with the KaleidaGraph software (Version 3.6; Hulinks Inc.).

Results and Discussion

Water Sorption Behavior

The water sorption behavior of the samples is shown in Fig. 1. The values with the results of the statistical analysis are also listed in Table S1 (supplemental data). The samples showed a sigmoidal curve typically observed in amorphous powders. Since amorphous glucose, maltose, and sorbitol readily crystallize [5], it is possible that the plasticizers may have crystallized during water sorption under a high a_w condition. However, it is thought that the plasticizers remained in an

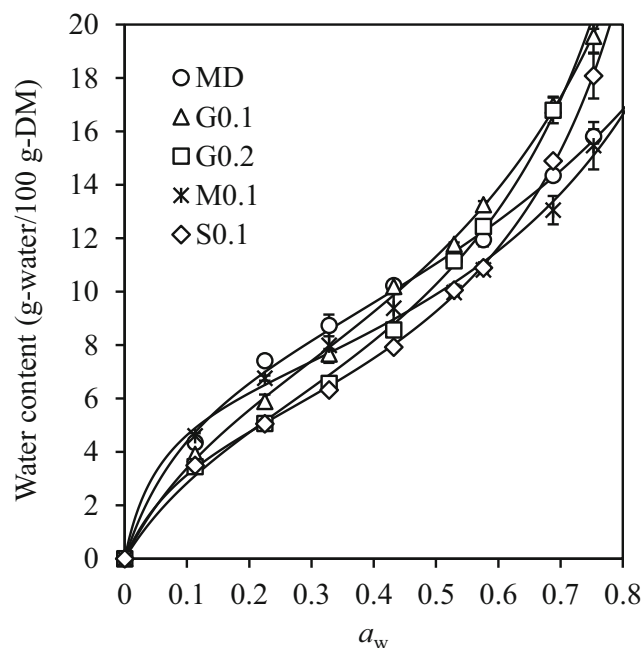


Fig. 1 Water sorption isotherm for freeze-dried carbohydrate blend powders at 25 °C. The values are expressed as mean \pm SD ($n = 3$). The solid line was obtained by the GAB fitting

amorphous state, because the water content of the samples did not decreased drastically as observed in the crystallization of maltose [25]. MD will have prevented the crystallization of amorphous plasticizers because of the formation of intermolecular hydrogen bonds between MD and plasticizers; the plasticizers are dynamically trapped in the amorphous MD matrix [26]. The water sorption isotherms could be analyzed using the GAB model (Eq. 1) with good regression parameters as listed in Table 1. The W_m and C decreased, and K increased by the addition of plasticizers (except for C in M0.1). Similar behavior was also reported for MD with DE = 12 [27], mixtures of maltopolymer–maltose [26], and hydrophobically modified starch–sucrose mixtures [28]. A comparison of W_m (monolayer water content) among MD, G0.1, and G0.2 revealed that the W_m decreased with increases in glucose content. At the same weight fraction of plasticizers, the W_m values were higher in the order of glucose > maltose > sorbitol. The reduction of W_m by the addition of plasticizers can be explained by the anti-plasticizing effect; plasticizers fill defects in the polymer, and thus, the hardness of the polymer can be mechanically strengthened [29–31]. Defects filled by plasticizers cause a reduction of water-binding sites in the polymer; consequently, W_m will be decreased by the addition of plasticizers to MD. The GAB parameters, however, are sensitive to the equilibrium water content at each a_w ; a small deviation in experimental data causes a large difference in the GAB parameters [24, 32]. Taking this fact into consideration, further discussion based on the GAB parameters was avoided in this study, and the GAB parameters were used to convert water content to a_w in the following section.

Glass Transition Behavior

As typical results, DSC thermograms (second scan) for MD, G0.1, and G0.2 having $a_w = 0.328$ are shown in Fig. 2. A clear endothermic shift due to glass transition was observed, and thus, T_g^{on} and T_g^{off} were determined from the onset and offset of the shift. At the a_w condition, the T_g^{on} decreased with increases in glucose content. This indicates that MD was plasticized by glucose because of the formation of intermolecular

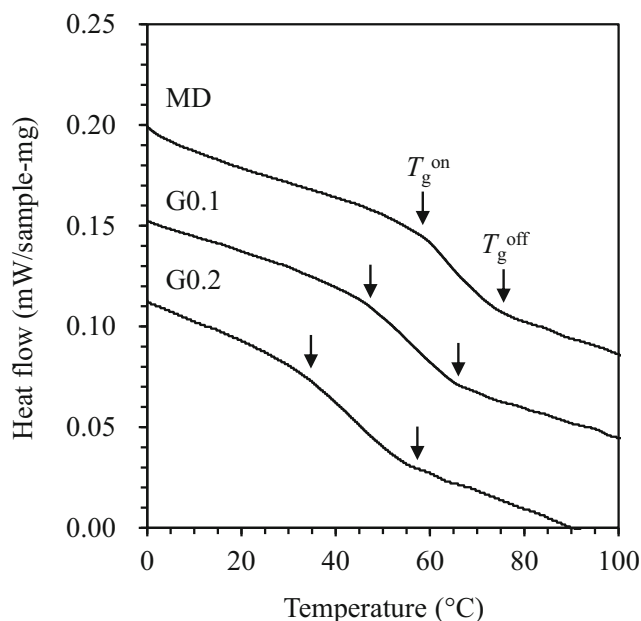


Fig. 2 Typical DSC thermograms for freeze-dried MD, G0.1 and G0.2 at $a_w = 0.328$ (second scanning). Onset and offset points of the endothermic shift were determined to be T_g^{on} and T_g^{off} , respectively

hydrogen bonds between MD and glucose; glucose partially cut the hydrogen bonds in amorphous MD matrix, and macroscopic molecular mobility increases [33]. In addition, the T_g range (temperature difference between T_g^{on} and T_g^{off}) increased with increases in glucose content. This suggests that distribution of the molecular mobility for MD was extended by glucose as a result of the heterogeneous formation of intermolecular hydrogen bonding [18, 19, 34, 35].

The effect of water content on the T_g^{on} and T_g^{off} of the samples is shown in Fig. 3. The values with the results of the statistical analysis are also listed in Tables S2 and S3 (supplemental data). From the results, it was confirmed that the T_g values decreased with increases in the water content because of the water plasticizing effect. The T_g curves (solid lines) were obtained by fitting of the Gordon-Taylor (GT) equation (Eq. 3) to the data:

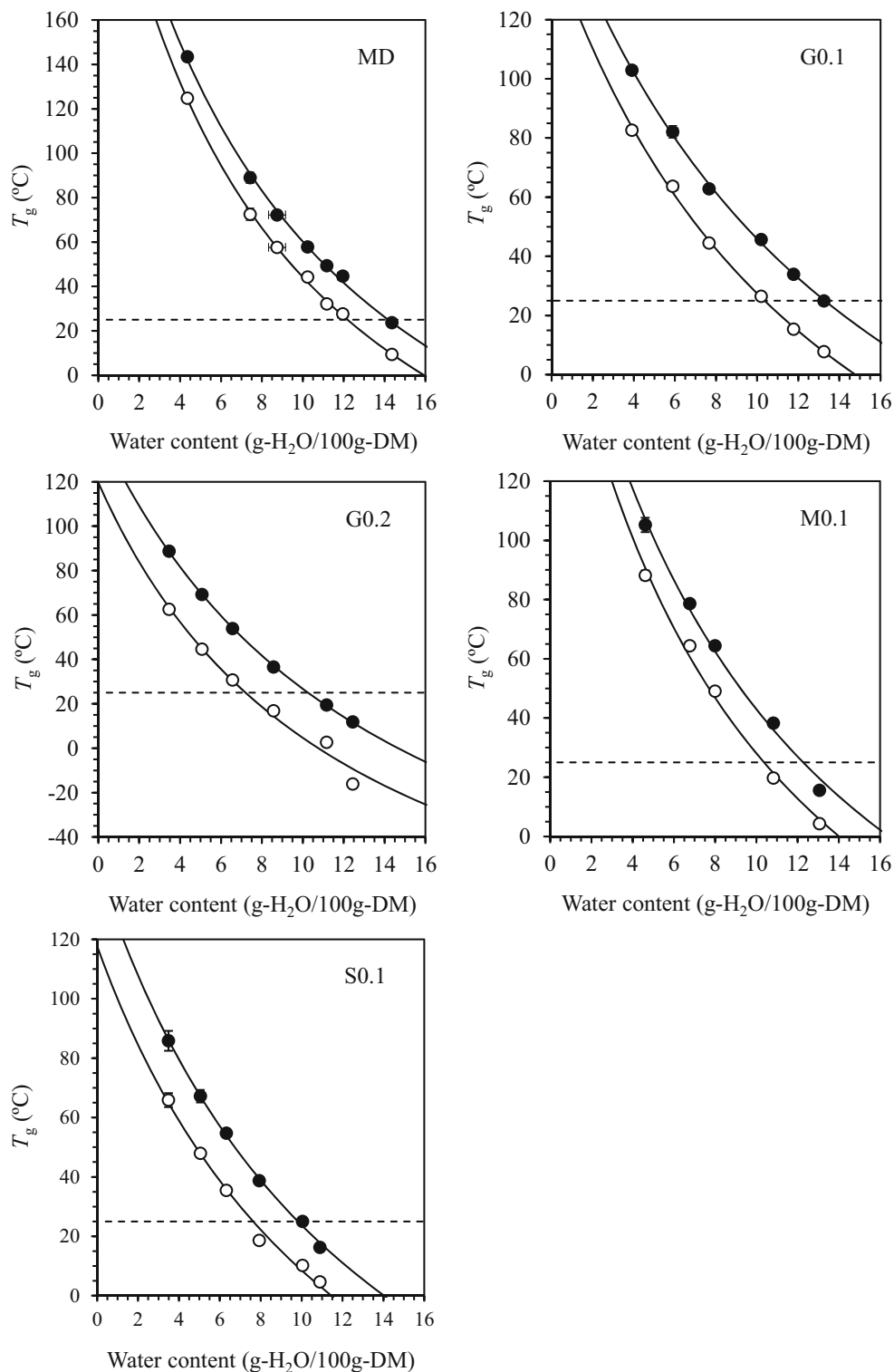
$$T_g = \frac{(1-X_w) \cdot T_{g(as)} + k \cdot X_w \cdot T_{g(w)}}{(1-X_w) + k \cdot X_w} \tag{3}$$

where X_w is the weight fraction of water, $T_{g(as)}$ and $T_{g(w)}$ are the T_g for anhydrous solute and pure water, respectively, and k is a constant. The $T_{g(w)}$ was set as 136 K in reference to previous reports [36, 37]. The $T_{g(as)}$ and k were provided as fitting parameters, and then, each T_g curve was obtained. From the T_g curve, the water content at $T_g = 25$ °C was determined as the critical water content (w_c). In addition, the w_c value was converted to critical water activity (a_{wc}) using the GAB equation (Fig. 1 and Table 1). These values ($T_{g(as)}$, k , w_c , and a_{wc}) were evaluated from T_g^{on} and T_g^{off} as listed in Table 2.

Table 1 GAB parameters for freeze-dried carbohydrate blend powders

	W_m (g/100 g-DM)	C	K	R^2
MD	8.67	12.93	0.649	0.997
G0.1	7.85	7.16	0.838	0.999
G0.2	6.47	6.40	0.933	0.999
M0.1	6.47	23.03	0.776	0.995
S0.1	5.37	10.72	0.950	1.000

Fig. 3 Effect of water content on the T_g^{on} and T_g^{off} for freeze-dried carbohydrate blend powders. The values are expressed as mean \pm SD ($n = 3$). The T_g curves were obtained by the GT fitting, and each w_c was determined as the water content at $T_g = 25^\circ\text{C}$



Isothermal Mechanical Relaxation

Isothermal mechanical relaxation measurement at 25°C is useful to validate the a_{w_c} determined by the fitting analysis mentioned above [9, 22]. In addition, the degree of mechanical relaxation reflects the molecular mobility [38]. Typical

isothermal mechanical relaxation curves are shown in Fig. 4. MD having $a_w = 0.113$ showed a small mechanical relaxation because of its high elasticity, which is characteristic of the glassy state. In contrast, MD having $a_w = 0.753$ showed a large mechanical relaxation, suggesting a rubbery state. From the isothermal mechanical relaxation curve, ΔF (the

Table 2 T_g (anhydrous), k , w_c , and a_{wc} , for freeze-dried carbohydrate blend powders

	onset point					offset point				
	$T_{g(as)}$ (°C)	k	R^2	w_c (g/100 g-DM)	a_{wc}	$T_{g(as)}$	k	R^2	w_c (g/100 g-DM)	a_{wc}
MD	259.1	11.84	0.999	12.20	0.572	273.7	10.82	0.998	14.18	0.682
G0.1	145.7	7.19	0.998	10.36	0.456	163.6	6.43	0.999	13.29	0.580
G0.2	119.7	8.11	0.980	7.20	0.347	144.5	7.19	1.000	10.26	0.499
M0.1	199.9	10.4	0.994	10.37	0.531	214.3	9.52	0.993	10.27	0.637
S0.1	117.7	7.49	0.991	7.63	0.408	144.7	7.51	0.998	9.82	0.527

force difference between the initial compression and compression after 3 min) was evaluated.

The effect of a_w on the ΔF of samples is shown in Fig. 5. The vertical solid and dotted lines are a_{wc} values determined from T_g^{on} and T_g^{off} , respectively, hereafter referred to as a_{wc}^{on} and a_{wc}^{off} , respectively. The values with the results of the statistical analysis are also listed in Table S4 (supplemental data). The ΔF values of MD were low and almost constant (lower than 10 N) below a_{wc}^{on} , but increased drastically above a_{wc}^{on} and reached approximately 70 N at a_{wc}^{off} . These observations support that glass transition was caused by water sorption at a_{wc}^{on} and that molecular mobility remarkably increased under a rubbery state. Also, the ΔF values of G0.1, M0.1, and S0.1 showed almost similar behavior to those of MD; the ΔF values were lower than 10 N below a_{wc}^{on} , and increased above a_{wc}^{on} , and reached approximately 60 N at a_{wc}^{off} . It should be noted that the slopes of the ΔF - a_w plot

between a_{wc}^{on} and a_{wc}^{off} for G0.1, M0.1, and S0.1 were lower than that for MD. This result indicates that the distribution of molecular mobility for MD is extended by the addition of plasticizers. The tendency given by the plasticizers became even more remarkable in G0.2. This is supported by the recent rheological study of Dupas-Langlet et al. [39] who investigated the viscosity change above T_g for amorphous maltopolymer-maltose blends and reported that plasticizers extended the viscosity change depending on the amount of addition.

Caking Behavior

Although caking behavior depends on experimental conditions such as the mass, size, and shape of powder particles, temperature and time of storage, and speed and amplitude of sieving [7, 40–44], caking behavior under identical conditions gives valuable knowledge on the physical stability of amorphous food powders [9, 24]. The effect of a_w on the degree of caking for the samples is shown in Fig. 6. The vertical solid and dotted lines indicate a_{wc}^{on} and a_{wc}^{off} , respectively. The values with the results of the statistical analysis are also listed in Table S5 (supplemental data). The degree of caking for MD was negligible below a_{wc}^{on} , but increased drastically above a_{wc}^{on} and reached 100% at an a_w that was close to a_{wc}^{off} . The degree of caking for G0.1, M0.1, and S0.1 was also negligible below their a_{wc}^{on} , but increased remarkably above a_{wc}^{on} and reached 100% at around a_{wc}^{off} . The dependence of the degree of caking on a_w became slightly broader because of the large a_w range between a_{wc}^{on} and a_{wc}^{off} . This observation was emphasized for G0.2. Taking the ΔF -rising behavior into account, the caking behavior for plasticizer-added samples can be corresponded to the extended distribution of molecular mobility. The present results corroborate the fact that caking occurs at T and a_w conditions above T_g^{on} [6–9, 13, 16, 24, 40]. However, T_g^{on} is not always a critical indicator of the caking behavior because of heterogeneous molecular mobility. T_g^{off} and a_{wc}^{off} can be applied to better predict caking as discussed in the following section.

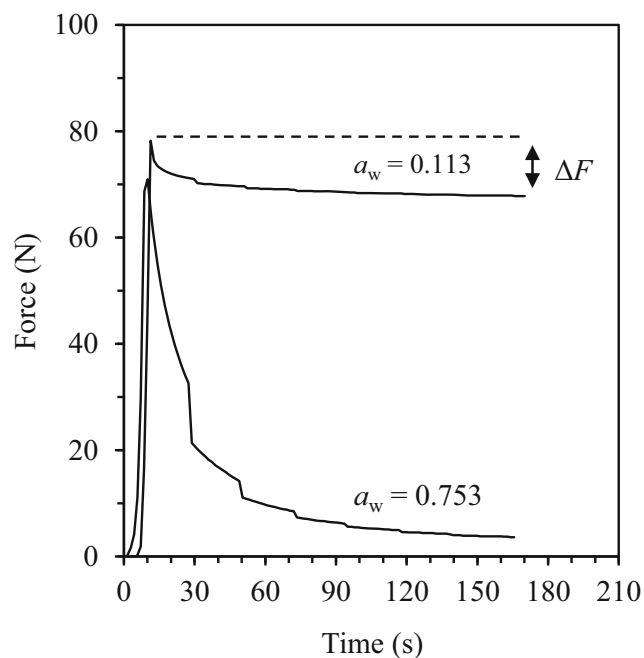
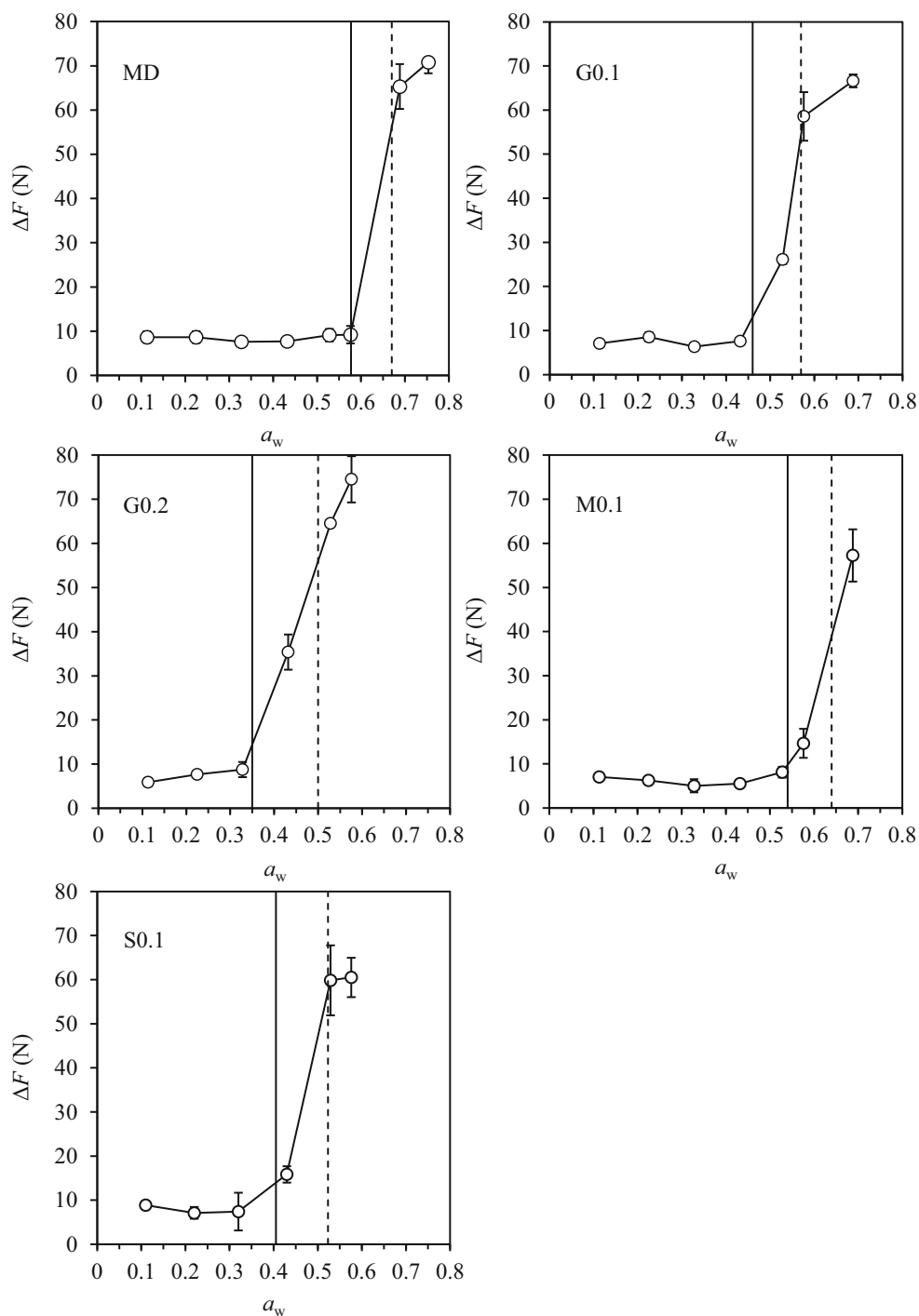


Fig. 4 Typical mechanical relaxation behavior for freeze-dried MD powders

Fig. 5 Effect of a_w on the ΔF for freeze-dried carbohydrate blend powders. The values are expressed as mean \pm SD ($n = 3$). The vertical solid and dotted lines are a_{wc}^{on} and a_{wc}^{off} , respectively



Predictions of Viscosity and Caking Behavior Based on T_g Range

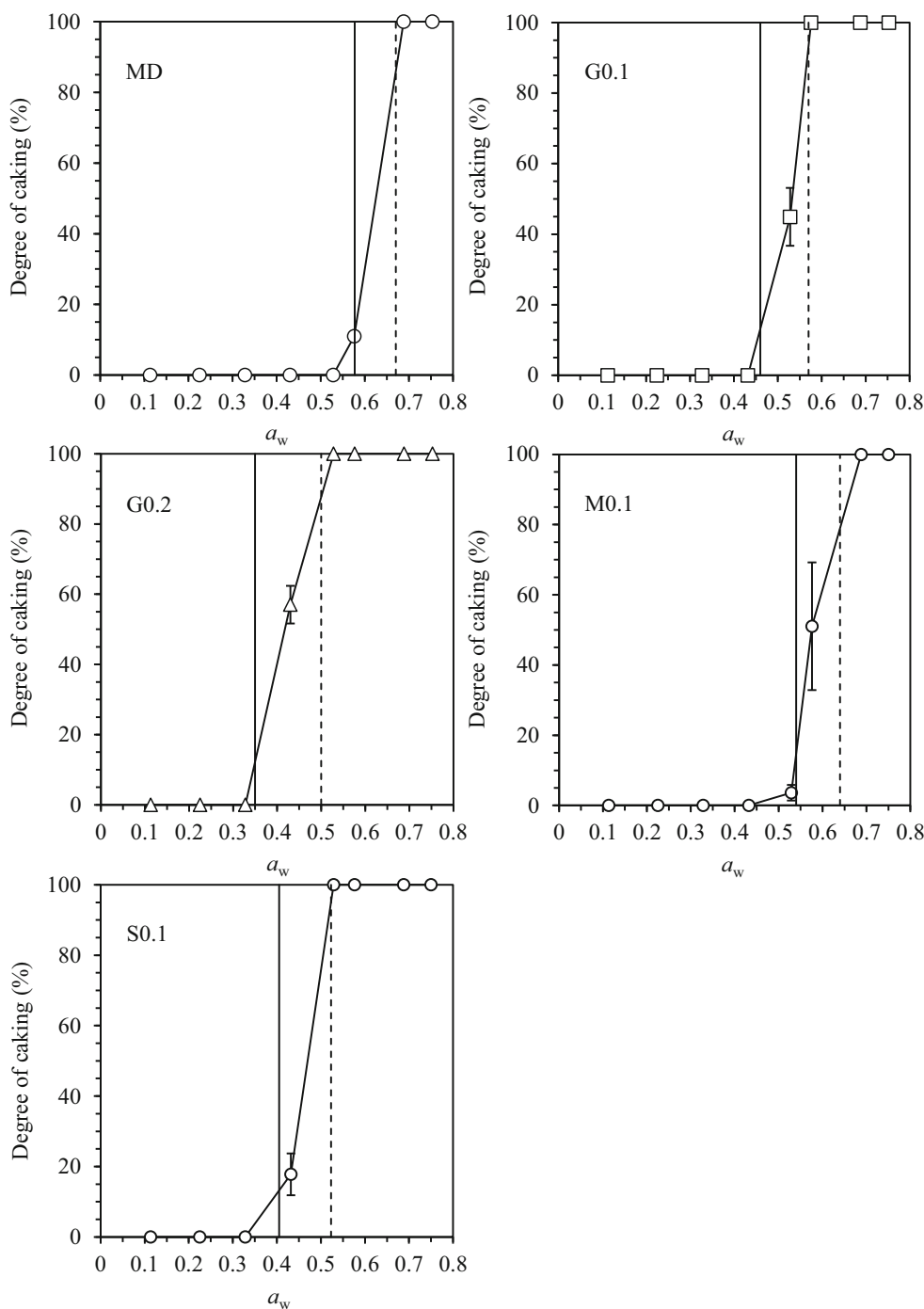
It is known that the T_g range reflects the distribution of molecular mobility [45]; the larger the T_g range, the broader the expected distribution of molecular mobility. The broad distribution of molecular mobility reflects a gradual dependence of viscosity (η) on temperature near T_g [11]. The dependence of η

on temperature can be described by the Vogel–Fulcher–Tamman (VFT) equation (Eq. 4):

$$\eta = \eta_0 \exp\left(\frac{DT_0}{T - T_0}\right) \quad (4)$$

where η_0 (Pa·s) is the viscosity at infinite temperature, T_0 (K) is the temperature of viscosity divergence, and D

Fig. 6 Effect of a_w on the degree of caking for freeze-dried carbohydrate blend powders. The vertical solid and dotted lines are a_{wc}^{on} and a_{wc}^{off} , respectively. The values are expressed as mean \pm SD ($n = 3$)

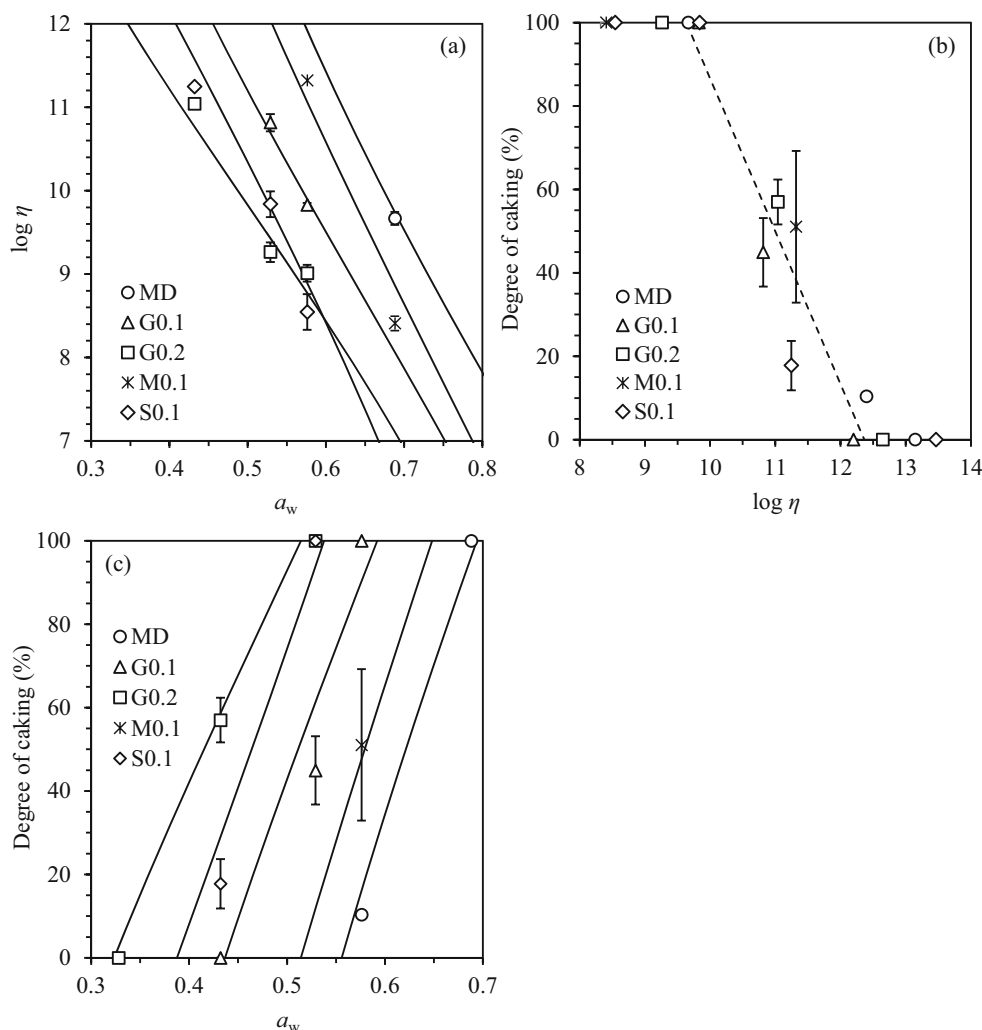


(dimensionless) is a constant described as “strength parameter” [46]. D characterizes the dependence of η on temperature; the higher the D , the broader the dependence of η on temperature. When T_g^{on} and T_g^{off} are applied to Eq. 4, Eq. 4 can be described as:

$$\frac{\ln \eta_g^{on} - \ln \eta_0}{\ln \eta_g^{off} - \ln \eta_0} = \frac{T_g^{off} - T_0}{T_g^{on} - T_0} \tag{5}$$

where η_g^{on} and η_g^{off} are η at T_g^{on} and T_g^{off} , respectively. It is known that η_0 and η_g^{on} can be empirically applied as 10^{-5} Pa·s and 10^{12} Pa·s, respectively [46]. The η_g^{off} , on the other hand, depends both on the temperature dependence of η and on the heating rate in DSC measurement [11]. The greater the dependence of η on temperature and the higher the DSC heating rate, the higher the T_g^{off} (the lower the η_g^{off}). When η_g^{off} is regarded as a constant at each DSC heating rate, T_0 can be estimated from the experimentally determined T_g^{on} and T_g^{off}

Fig. 7 **a** Dependence of η on a_w at 25 °C of freeze-dried carbohydrate blend powders. **b** Effect of the predicted η on the degree of caking for freeze-dried carbohydrate blend powders. **c** Degree of caking of freeze-dried carbohydrate blend powders as a function of a_w



from Eq. 5. On the other hand, when $\eta_0 = 10^{-5}$ Pa·s and $\eta_g^{on} = 10^{12}$ Pa·s are applied to Eq. 4, Eq. 4 can be described as:

$$D = \frac{\ln 10^{17} (T_g^{on} - T_0)}{T_0} \tag{6}$$

From the experimentally determined T_g^{on} and the calculated T_0 , D can be estimated by Eq. 6. As a result, the dependence of η on temperature can be predicted by Eq. 4.

It is reported that anhydrous sucrose has approximately $D \approx 6.0$ [46]. In our preliminary study, the T_g^{on} and T_g^{off} for anhydrous sucrose observed at 5 °C/min (same DSC scanning condition as this study) were determined to be 341.4 K and 348.0 K, respectively (data not shown). When $\eta_0 = 10^{-5}$ Pa·s and $\eta_g^{on} = 10^{12}$ Pa·s were applied to Eq. 5, η_g^{off} was estimated to be $10^{9.8}$ Pa·s. This value was in good agreement with the η_g^{off} for inorganic glasses reported previously [11].

Based on the η_g^{off} value, the dependence of η on temperature could be calculated for the MD–plasticizer blend powders. The T_g^{on} and T_g^{off} were described as a function of water

content by the GT equation (Eq. 3) according to Fig. 3. In addition, water content was converted to a_w using the GAB equation (Eq. 1) according to Fig. 1. Combining Eqs. 1, 3, and 4, the dependence of η on a_w at 25 °C was calculated as shown in Fig. 7a. The slope of $\log \eta$ versus the a_w curve is affected by the T_g range. Notably, G0.2 has a crossover a_w point with S0.1 because of the difference in the T_g range. The effect of the predicted η on the degree of caking for the samples is shown in Fig. 7b. The degree of caking linearly increases with decreases of the predicted $\log \eta$ in the η range between approximately 10^{12} Pa·s and 10^{10} Pa·s. From the linear regression, an empirical formula (Eq. 7) could be obtained with a good coefficient of determination ($R^2 = 0.8475$) as follows:

$$\text{Degree of caking (\%)} = -41.27 \cdot \log \eta + 502.1 \tag{7}$$

The degree of caking (%) and $\log \eta$ (Pa·s) ranged between 0 and 100, and 9.64 and 12.36, respectively. According to Eq. 7, the degree of caking could be described as a function of a_w as shown in Fig. 7c. The proposed approach is unique in that it

demonstrated that the dependence of η on temperature and a_w is characterized by the T_g range. This will be useful as a better predictive approach for caking of carbohydrate blend powders based on T_g^{on} and T_g^{off} .

It should be pointed out that caking is a time-dependent phenomenon [6, 41, 42]. Although the degree of caking was evaluated at the storage time of 1 week in this study, the values will increase more or less with longer storage times. In addition, particle size and shape (contact between particles) affect caking [13, 14, 47, 48]. As mentioned above, dispersions (semi-crystalline starch and water-insoluble fiber) undermine the hardness of the cake structure. The effect of these factors on the proposed predictive approach will be investigated in the next study.

Conclusion

The water sorption, glass transition, and caking behaviors of freeze-dried MD-carbohydrate plasticizer blend powders were investigated. In order to characterize the viscosity change at a higher temperature than T_g^{on} , T_g^{on} and T_g^{off} were evaluated from DSC thermograms. In addition, T_g^{on} and T_g^{off} were corresponded to a_w^{on} and a_w^{off} , respectively, through the water sorption behavior. It was suggested that the temperature difference between T_g^{on} and T_g^{off} and the a_w difference between a_w^{on} and a_w^{off} reflected the distribution of molecular mobility above the T_g . Isothermal mechanical relaxation behavior supported this suggestion. The distribution of molecular mobility affected the degree of caking. In reference to a previously suggested approach, T_g^{on} and T_g^{off} were converted to viscosity, and a predictive approach in consideration of the dependence of viscosity on water activity was proposed. For better prediction, it is necessary to understand the effects of storage time, particle size and shape, and water-insoluble materials (dispersions) on the degree of caking. These are future subjects of study.

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Compliance with Ethical Standards

Conflict of Interest Kiyoshi Kawai (corresponding author) received a collaborative research fund from San-ei Surochemical Co., Ltd. (Aichi, Japan) for a different purpose from this study.

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