

Effect of Water Content on the Glass Transition Temperature of Calcium Maltobionate and its Application to the Characterization of Non-Arrhenius Viscosity Behavior

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Abstract To understand the fundamental physical properties of calcium maltobionate (MBCa), its water sorption isotherm, glass transition temperature (T_g), and viscosity (η) were investigated and compared with those of maltobionic acid (MBH) and maltose. Although amorphous maltose crystallized at water activity (a_w) higher than 0.43, MBCa and MBH maintained an amorphous state over the whole a_w range. In addition, MBCa had a higher T_g and greater resistance to water plasticizing than MBH and maltose. These properties of MBCa likely originate from the strong interaction between MBCa and water induced by electrostatic interactions. Moreover, the effects of temperature and water content on η of an aqueous MBCa solution were evaluated, and its behavior was described using a semi-empirical approach based on a combination of T_g extrapolated by the Gordon-Taylor equation and a non-Arrhenius formula known as the Vogel-Fulcher-Tammann equation. This result will be useful for understating the effect of MBCa addition on the solution's properties.

Keywords Amorphous · Water sorption isotherm · Glass transition temperature · Differential scanning calorimetry · Water plasticizing

Introduction

Maltobionic acid (MBH) is a type of aldonic acid in which glucose and gluconic acid are linked via an α -1,4-glycosidic bond; it is obtained from the chemical or enzymatic oxidation of maltose [1, 2]. MBH has antioxidant/chelation, barrier strengthening, and moisturizing effects, and it is commonly used in cosmetics products [3]. Moreover, maltobionate can form various types of salts depending on the cation used. Among those, calcium maltobionate (MBCa) is expected to be an effective calcium soluble material for use in pharmaceutical and food products because of its high water solubility and mild bitter taste.

MBCa powder is amorphous and thus readily adsorbs moisture and aggregates during processing and preservation. It is known that aggregation of an amorphous powder can be explained via glass transition effects [4, 5]. At a temperature below the glass transition temperature (T_g), the amorphous powder is in a glassy state and behaves as a physically stable powder. Above T_g , the amorphous powder is in a rubbery state. As rubbery materials have viscoelastic properties, the fluidity of the powder is lost and it aggregates into a solid. T_g of hydrophilic amorphous materials decreases with increasing water content because of water plasticizing [6–12]. Therefore, glass transition can occur in an amorphous powder held at a constant temperature when its water content is increased by water sorption.

When MBCa is used as an aqueous solution, viscosity (η) is treated as an important physical parameter for drying operation [13, 14] and quality control of liquid food [15, 16]. Similar to T_g , η of an aqueous solution depends on temperature and water content [17]. The effect of temperature on η of a solution can be described by Arrhenius formula in a limited temperature range; however, it deviates from Arrhenius behavior at low temperatures near T_g [18]. To understand the effect of temperature on η of solutions over the whole

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temperature range, a non-Arrhenius formulation that is applicable around T_g has often been employed [17–21]. These results suggest that the effect of water content on η of solutions will also correspond to the T_g curve.

As mentioned above, water sorption, glass transition, and viscosity are practically important parameters for amorphous hydrophilic materials. Although there have been many studies on the subject, MBCa has not yet been investigated to the best of our knowledge. The purpose of this study thus was to understand the water sorption isotherm (water content versus a_w) and the T_g -curve (T_g versus water content) of the MBCa powder, and the effects of temperature and water content on η of MBCa aqueous solutions. For comparison, water sorption isotherm and the T_g -curve of amorphous MBH and maltose were also investigated.

Materials and Methods

Sample Preparation

For the preparation of MBH and MBCa, reagents (analytical grade) of maltose monohydrate, calcium carbonate, catalase, and glucose oxidase were purchased from Wako Pure Chemical Industries, Ltd. (Tokyo, Japan) and/or Amano Enzyme Inc. (Aichi, Japan). A 30 % (w/v) maltose solution (1000 mL) was reacted with 900 U of glucose oxidase, 60,000 U of catalase, and 55 g of calcium carbonate at 35 °C with aeration (1 L/min) and agitation (500 rpm). For MBCa purification, an activated carbon treatment at 80 °C for 30 min was carried out, and then the active carbon and enzymes were removed using vacuum filtration with Whatman glass microfiber filters, Grade GF/F, and membrane filters with a mixed cellulose ester pore size of 0.2 μm (Whatman Inc., USA). For MBH purification, the MBCa solution was desalted by cation exchange resin (Dowex88, Dow Chemical Company, USA) and decolorized mixed bed of anion (WA30, Mitsubishi Chemicals, Tokyo) and cation-exchange resins (Dowex88, Dow Chemical Company, USA). The eluate was concentrated in a rotary evaporator (RE1-D, AGC TECHNO GLASS CO., LTD. Japan). It was preliminarily confirmed that the purity of the MBH and MBCa solutions was more than 99 % by HPLC. In order to obtain freeze-dried maltose, MBH, and MBCa, a 10 % (w/w) solution (10 mL) was prepared in a glass vial and then placed in a freezer. The frozen preparation was set on the pre-cooled stage of the freeze-drier and vacuumed at a pressure below 70 Pa while increasing the temperature from -35 °C to 5 °C over a period of 2.5 days. The obtained samples were hermetically stored in the vial.

Isothermal Water Sorption

The MBCa, MBH, and maltose samples were vacuum-dried at 80 °C for 8 h; the fully dried samples were then held under

various water activity (a_w) conditions at 25 °C. a_w was adjusted with saturated salts: LiCl ($a_w = 0.11$), CH_3COOK ($a_w = 0.23$), MgCl_2 ($a_w = 0.33$), K_2CO_3 ($a_w = 0.43$), $\text{Mg}(\text{NO}_3)_2$ ($a_w = 0.53$), NaBr ($a_w = 0.58$), NaCl ($a_w = 0.75$), KCl ($a_w = 0.84$), and KNO_3 ($a_w = 0.94$). The equilibrium of water sorption was confirmed gravimetrically. A portion of each sample was used for DSC measurements. The remaining portions of each sample were used to measure the water content. Hydrated samples were dehydrated at 105 °C for 16 h, and their water content was evaluated gravimetrically. The measurements were performed in duplicate, and the results were averaged.

DSC Measurement

Glass transition of the MBCa, MBH, and maltose samples was investigated using DSC (DSC120; Seiko Instruments Inc., Tokyo, Japan). The water content of the samples was adjusted under various a_w conditions as mentioned above. Alumina was used as a reference, and the temperature and heat flow were calibrated using indium and distilled water.

The sample (4–10 mg) was placed in an aluminum pan and then hermetically sealed. To evaluate anhydrous T_g of MBCa, MBH and maltose, the samples were placed into the DSC pan and held at 105 °C for 1–6 h and then hermetically sealed [22]. DSC measurements were conducted at 5 °C/min in a temperature range between 0 °C and 180 °C. Glass transition is observed as an endothermic shift in a DSC thermogram. However, glass transition observed in the first scan shows an endothermic peak because of the enthalpy relaxation effect depending on the thermal history of glassy samples; the T_g value may be affected by the enthalpy relaxation effect to various degrees. To cancel the thermal history of glassy samples on T_g , DSC measurements were conducted again after the first scan and then T_g was evaluated from the onset point of the endothermic shift observed in the second scan [22–24]. The T_g measurements were performed in duplicate, and the results were averaged.

Viscosity

MBCa was directly mixed with distilled water in the glassy vial, and 10 %–60 % (w/w) MBCa aqueous solution samples were prepared. Viscosity was investigated using viscometer (Haake Mars III system; Thermo Fisher Scientific Inc., Kanagawa, Japan). A corn plate ($\varphi = 60$ mm, 1°) was employed, and the shear rate (1/s) was investigated by shear stress of up to 100 Pa. The temperature was adjusted between -5 °C and 45 °C. The measurements were performed in triplicate, and the results were averaged.

Results and Discussion

Water Sorption Isotherm

Water sorption isotherms (25 °C) for MBCa, MBH, and maltose are shown in Fig. 1. The water content of MBCa and MBH increased with a_w , and the behavior showed a sigmoidal curve over the whole a_w range. Amorphous maltose, on the other hand, showed an abrupt decrease of water content at $a_w > 0.43$. This indicates that amorphous maltose crystallizes during water sorption in a similar fashion to amorphous lactose [25]. From the result, it is noted that MBCa and MBH are more stable amorphous material than maltose. The solid lines for MBCa, MBH, and maltose were obtained by fitting the Brunauer–Emmett–Teller (BET) equation (Eq. 1) and the Guggenheim–Anderson–de Boer (GAB) equation (Eq. 2) to the sorption data, respectively.

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

$$W = \frac{W_m C K a_w}{(1-K a_w)(1-K a_w + C K a_w)} \quad (2)$$

where W , W_m , C , and K are the moisture content (g-H₂O/100 g-DM), the moisture content of the monolayer (g-H₂O/100 g-DM), a factor correcting the sorption properties of the first layer with respect to the bulk liquid, and a factor correcting the properties of the multilayer with respect to the bulk liquid, respectively [26, 27]. For $K = 1$, the GAB equation is equivalent to the BET equation. Eq. 1 and Eq. 2 have been used for the water sorption analysis up to $a_w = 0.45$ and for the whole range ($a_w = 0-1$), respectively [28–32]. Maltose was analyzed using Eq. 1 because crystallization occurred at a higher a_w than 0.43. On the contrary, MBCa and MBH were

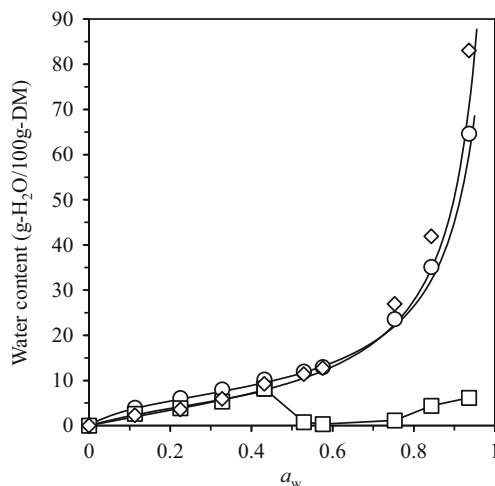


Fig. 1 Water sorption isotherm for MBCa (circle), MBH (diamond), and maltose (square) at 25 °C

analyzed using both of Eq. 1 ($a_w \leq 0.43$) and Eq. 2 ($a_w \leq 0.94$) to understand the water sorption behavior. The obtained parameters (W_m , C , and K) are listed in Table 1. The W_m and C values of BET were slightly different from those of GAB, because their parameters were affected by K value of GAB [32]. GAB gave better fitting results ($R^2 > 0.952$) than BET did ($R^2 > 0.662$). In the comparison of GAB parameters between MBCa and MBH, there were minor differences of W_m and K values. It is noted that MBCa has the highest C among them. This is likely related to the electrolytic dissociation of MBCa; ionized groups hydrate strongly [33] and form hydration shells with water molecules; further, calcium ions can interact with six water molecules [34].

T_g -curve

Typical DSC thermograms (second scan) for the MBCa samples are shown in Fig. 2. The MBCa samples showed an endothermic shift owing to glass transition, and the T_g value was evaluated from the onset point of the shift. The anhydrous sample ($a_w = 0$) showed an exothermic peak at a higher temperature than T_g . This originated from the thermal decomposition of MBCa.

The obtained T_g was plotted against water content (g-H₂O/100 g-DM) as shown in Fig. 3. As expected, T_g decreased with an increase in water content. The solid line in Fig. 3 was obtained by fitting the Gordon–Taylor (GT) equation (Eq. 3) to the T_g data,

$$T_g = \frac{W_s T_{gs} + k W_w T_{gw}}{W_s + k W_w} \quad (3)$$

where T_{gs} (K) and T_{gw} (K) are the T_g values of the anhydrous solute (MBCa, MBH, and maltose) and water, W_s and W_w are the mass fractions of the solute and water, and k is a constant depending on the system. The k value indicates the sensitivity to water plasticizing [8]; the higher the k value, the greater the water content dependence of T_g . Both T_g and T_{gs} were determined experimentally. T_{gw} was set to 136 K as determined in previous publications [35, 36], and k was obtained as a fitted parameter. The GT parameters (T_{gs} and k) are also listed in Table 1. From these results, glass transition induced by water sorption at a constant temperature could be

Table 1 GAB and GT parameters for MBCa, MBH, and maltose

	BET		GAB			GT	
	W_m	C	W_m	C	K	T_{gs}	k
maltose	5.59	4.75	-	-	-	368.6	7.4
MBH	7.58	2.46	6.93	2.75	0.967	346.9	4.7
MBCa	6.68	8.55	6.45	9.19	0.954	421.3	5.7

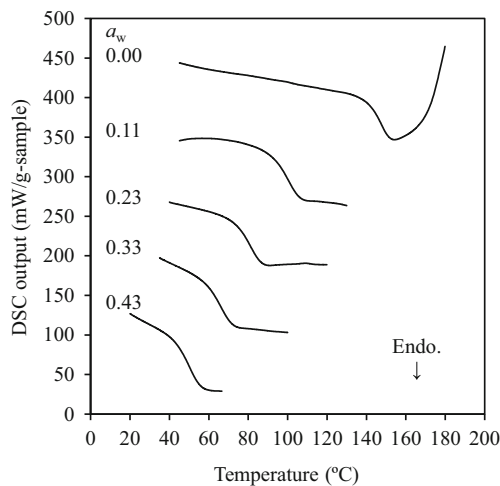


Fig. 2 Typical DSC thermograms for MBCa samples

evaluated. From Fig. 3, the water content at which MBCa, MBH, and maltose showed $T_g = 25^\circ\text{C}$ (critical water content) was determined to be 13.3 g-H₂O/100 g-DM, 6.41 g-H₂O/100 g-DM, and 5.86 g-H₂O/100 g-DM, respectively. Their critical water contents were also matched to $a_w = 0.56$, 0.37, and 0.35, respectively, using Eq. 1 or Eq. 2. At a higher critical water content or a_w , the amorphous powder products became physically unstable; there was a risk of aggregation and recrystallization during storage [4, 5, 13, 14]. Considering this, it is concluded that MBCa is a more stable glassy material than MBH and maltose.

The T_{gs} of maltose was evaluated to be 95.5°C . This value was almost equivalent to previous reports given by other researchers ($90 \sim 97^\circ\text{C}$ [37–40]) and by another technique (90°C by FT-IR [40]). The minor variation of the T_{gs} appeared in the literature will be caused by the fact that glass transition is a relaxation phenomenon of amorphous materials; T_g depends more or less on the preparing method [41] and measuring condition [42, 43].

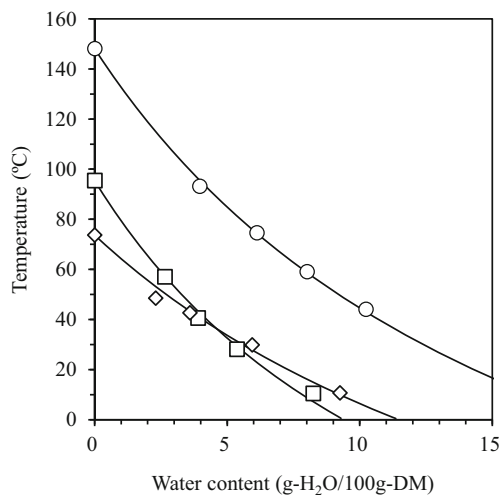


Fig. 3 T_g curves for MBCa (circle), MBH (diamond), and maltose (square)

The T_{gs} of MBH (73.7°C) was lower than maltose (95.5°C). This indicates that oxidation reduces the T_{gs} of maltose as similar to reduction; the T_{gs} of maltitol is reported to be 47.3°C [44]. Similar effect of reduction on the T_{gs} of saccharide is also confirmed in the comparison between glucose ($37 \sim 38^\circ\text{C}$) and sorbitol ($-1.9 \sim 0^\circ\text{C}$), lactose (112°C) and lactitol (54.9°C), and matrotriose (134°C) and maltotriitol (88.6°C), respectively [37, 44]. On the other hand, MBCa (148.1°C) had a much higher T_{gs} than maltose, maltitol, and MBH. Similar effects of oxidation and Ca-addition on the glass transition properties are expected to other saccharides; for example, T_{gs} s of calcium gluconate (103°C) and calcium lactobionate (137°C) are much higher than that of glucose and lactose [45].

It is known that T_{gs} of carbohydrate materials increases with molar weight (MW) or formula weight (FW) because of the enhancement of intermolecular interactions [22]. One of the reasons why MBCa had a high T_{gs} is likely that MBCa (FW = 754) has a much higher weight than MBH (MW = 358), maltitol (MW = 344), and maltose (MW = 342). In comparison with glucan, it should be noted that MBCa has an equivalent T_{gs} to maltohexaose (MW = 991) [40]. In addition, it is known that Ca^{2+} can elevate the T_g of hydrogen-bonding system because of thermally reversible self-polymerizing [46].

MBCa and MBH had a lower k (greater resistance to water plasticizing) than maltose. It is known that k of mono- and disaccharide increases linearly with increasing T_{gs} ($^\circ\text{C}$) and the relationship is empirically expressed as follows [8]:

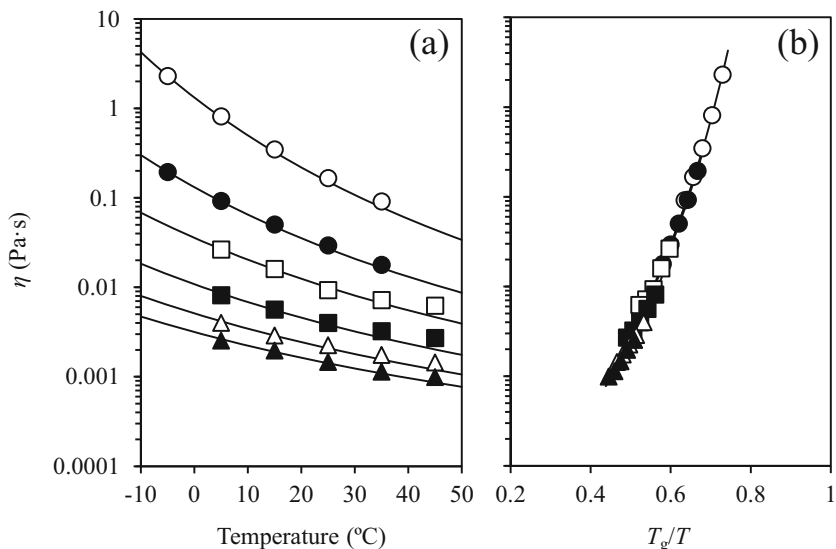
$$k = 0.0293 T_{gs} + 3.61 \quad (4)$$

In fact, it was confirmed that $k = 7.4$ for maltose and $k = 4.7$ for MBH are relatively in a good agreement with the value calculated by Eq. 4 ($k = 6.4$ for maltose and $k = 5.8$ for MBH). On the other hand, $k = 5.7$ for MBCa differed significantly from the calculated value ($k = 7.9$). As mentioned above, the lower the k value, the greater the resistance to water plasticizing. From these results, it was concluded that MBCa has a high T_g and large resistance to water plasticizing. This property is similar to that of oligo- and polysaccharides. For example, it is known that for amorphous inulin T_g increases from 111°C to 141°C and k decreases from 6.4 to 5.2 with an increase in the average molar mass between 1197 g/mol and 4395 g/mol [22]. The high T_g and low k of MBCa likely originates from the strong interaction between MBCa and water induced by electrostatic interactions.

Effects of Temperature and Water Content on η of MBCa

Every MBCa aqueous solution exhibited Newtonian behavior; thus, η (Pa·s) was evaluated from the linear relationship

Fig. 4 Effect of temperature on η of MBCa aqueous solution for each solute content (a) and T_g -scaled Arrhenius plot (b), open circle: 60 %, closed circle: 50 %, open square: 40 %, closed square: 30 %, open triangle: 20 %, and closed triangle: 10 % (w/w)



between shear stress and shear rate (data not shown). The effect of temperature on η of each aqueous MBCa sample is shown in Fig. 4a. As mentioned above, the effect of temperature on η of an aqueous solution can be described by the Arrhenius formula in a limited temperature range, but it deviates for temperatures near T_g . Over the whole temperature range, the dependence of η on temperature can be described instead by the Vogel–Fulcher–Tammann (VFT) equation (Eq. 5):

$$\eta = \eta_0 \exp\left(\frac{DT_0}{T - T_0}\right) \tag{5}$$

where η_0 (Pa·s), D (dimensionless), and T_0 (K) were constants [18]. It is known that η_0 is approximately 10^{-5} Pa·s [18]. On the other hand, T_g is known to be the temperature at which η becomes approximately 10^{12} Pa·s [18]. When these values

are input into Eq. 5, D can be empirically represented as a function of T_g and T_0 (Eq. 6).

$$D = \frac{39.14(T_g - T_0)}{T_0} \tag{6}$$

T_g of the aqueous MBCa sample cannot be evaluated experimentally because water crystallizes before the system falls into the glassy state during the cooling process. Therefore, T_g was extrapolated through Eq. 3 in this study. When the extrapolated T_g was input into Eq. 6, D could be described as a function of T_0 . Thus, the only unknown parameter in Eq. 5 was T_0 and then the solid lines in Fig. 4a were obtained by fitting Eq. 5 to the η data. In addition, effect of temperature on the η for MBCa aqueous solution (Fig. 4a) was described as a T_g -scaled Arrhenius plot (i.e. Angell plot) in Fig. 4b. From the result, it was confirmed that effect of temperature of the η for MBCa aqueous solution was roughly described by a master

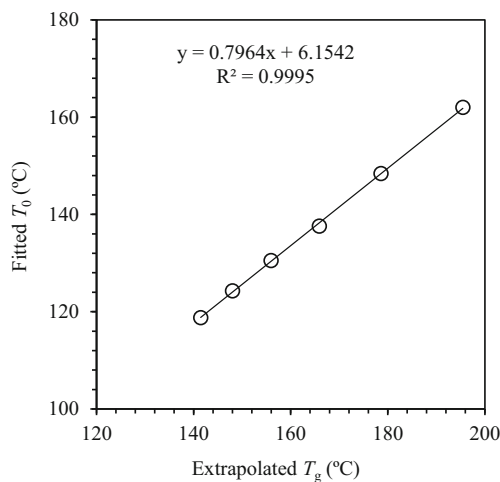


Fig. 5 Relation between T_g and T_0 for each MBCa aqueous solution. T_g and T_0 were given by GT and VFT equations, respectively

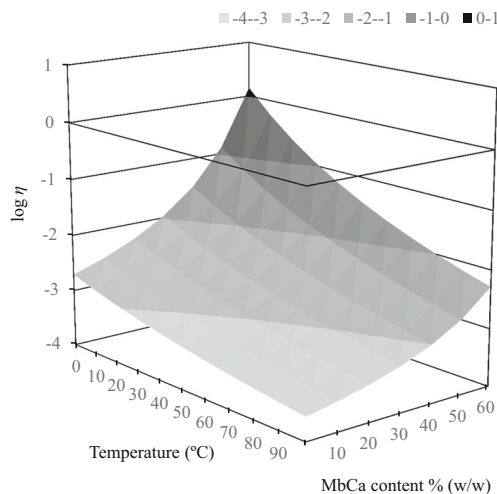


Fig. 6 Predicted η for MBCa aqueous solution described as functions of temperature and water content

curve (Fig. 4b). Similar results were also reported for maltose, trehalose, and trehallose-borax aqueous solutions [17, 21, 47].

From the fitting results, it was noted that T_0 increased with decreasing water content of MBCa, which was similar to the trend in T_g . This observation agreed with trehalose aqueous solution [17]. To understand the relation between T_g and T_0 , T_0 was plotted against T_g in this study, and then a linear relationship was obtained (Fig. 5). As mentioned above, T_g is the temperature at which η becomes 10^{12} Pa·s. On the other hand, T_0 is the temperature of viscosity divergence (i.e., $\eta = \infty$) [18]. Since both of T_g and T_0 have a similar physical meaning of which viscosity becomes the certain value, it is reasonable that T_g has a linear proportion to T_0 . The T_g of water was 136 K [35, 36], and thus the linear relation shown in Fig. 5 gave $T_0 = 115$ K. When the η data of water in the temperature range between 0 °C and 100 °C (11 points) were taken from a general chemical handbook, it was found that the parameters well described the dependence of η on temperature ($R^2 = 0.9962$). This fact supports the validity of the empirical linear relation for the prediction of T_0 from T_g .

From the relationship between T_0 and T_g , it is noted that the temperature difference between T_g and T_0 decreased with increase water content (with decrease T_g). In addition, the D calculated by Eq. 6 decreased from 8.1 (60 % MBCa) to 7.5 (10 % MBCa). Similar effect of water content on the D is reported for sucrose [18]. It is known that D can be related to strong-fragile classification of liquid. Effect of temperature on the η of strong liquid shows Arrhenius-like behavior. In contrast, the lower D , the greater non-Arrhenius behavior is observed; such a liquid is described as “fragile liquid”. It is commonly known that hydrogen-bonding system is classified into fragile liquid. For example, D values for sucrose and trehalose aqueous solutions are reported to be approximately 6 [18] and 3.32 ~ 4.85 [17], respectively. MBCa aqueous solution is slightly stronger liquid than these saccharides. Water, on the other hand, shows irregular strong/fragile behavior; fragile behavior at a higher temperature than 236 K (limitation of supercoiling), but strong behavior at a temperature near T_g (in the temperature range between 136 K and 150 K) are observed [18, 36]. Although further discussion on the molecular dynamics of water is avoided in this paper, it is emphasized that water showed fragile behavior in the temperature range between 273 K and 373 K. Consequently, the reason why the D of MBCa aqueous solutions decreased with increase in water content will be that strong liquid-structure formed by MBCa was destructed by fragile liquid (i.e., water).

When T_0 is treated as a function of T_g according to Fig. 5, effects of temperature and water content on η of MBCa can be predicted from the combination of Eqs. 3, 5, and 6; T_0 and D of Eq. 5 can be replaced by T_g , and T_g can be described as a function of water content by Eq. 3. The combined equation gives a three-dimensional diagram as shown in Fig. 6. As

mentioned above, η is an important physical parameter for drying operation [13, 14] and quality control of liquid food [15, 16]. The diagram as shown in Fig. 6 will be useful for understating the effect of MBCa addition on the solution's properties. Taking the background of this predictive approach into account, the temperature range should be limited between 0 °C and 100 °C; water molecules exist as fragile liquid in the temperature range. In addition, MBCa content should be limited between 0 and 60 % (w/w); non-Newtonian behavior may be appeared at a higher MBCa content.

Conclusion

Water sorption, glass transition, and viscosity of MBCa were measured. These data are practically useful not only for the production of MBCa powder (drying operation and storage stability) but also for the quality prediction of food modified by adding MBCa. Because MBCa has the advantages of having a high T_g and great resistance to water plasticizing, MBCa will be a useful food modifier. In addition, a semi-empirical η -prediction approach based on T_g was proposed. To confirm the validity of this approach in more detail, it is necessary to apply it to many types of aqueous materials, which will be the subject of future studies.

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