Measuring Method of Glass transition Temperature using Aroma Sensor

Ratchanon Chantanuson[1], Jianlong Zhu[3], Hirokazu Shiga[2], Shuji Adachi[2], Apinan Soottitantawat[1] and Hidefumi Yoshii[3,*]

Abstract

Glass transition temperature (Tg) is very important to control the flavor release rate and the stability of functional compounds in spray-dried powder. Usually, Tg of wall material is measured by differential scanning calorimetry (DSC). However, it is very difficult to measure Tgs since the heat capacity changes of several compounds such as maltodextrin (MD) are so small. In this study, the simple method to measure Tg was proposed using aroma sensor. Spray dried powders of emulsified hexanol in middle chain triglyceride oil and hexanol containing other four flavors were formed with three kinds of wall materials, MD (dextrose equivalent=19), and two mixtures of MD and Fructose (Fr) (20wt% Fr and 80wt% MD, and 40wt% Fr and 60wt% MD). The release rate of hexanol from spray-dried powder was measured at the linear programmed temperature (ramping method) using an aroma sensor. The release rates of hexanol from spray-dried powder increased rapidly above the specific temperatures, which were the intercept temperatures of tangent line of hexanol release rates as the apparent glass transition temperatures for the wall materials. The apparent glass transition temperatures were similar values by the calculated temperature using Couchmann and Karasz equation. These results indicated the glass transition temperature could be estimated with flavor release measurement using aroma sensor at the linear programmed temperature.

Keywords: Glass transition temperature, Aroma sensor, Hexanol, Maltodextrin, Fructose.

[1] Center of Excellent in Particle Technology, Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University, Bangkok, 10330 Thailand

[2] Department of Agriculture and Food Technology, Faculty of Bio-environmental 11 Science, Kyoto Gakuen University, Kyoto, 621-0022 Japan

[3] Deparment of Applied Biological Science, Faculty of Agriculture, Kagawa University, Kagawa, 761-0701 Japan

* Corresponding author(s), e-mail: foodeng.yoshii@ag.kagawa-u.ac.jp

1. Introduction

Spray drying has been used for encapsulation process for a long time. That process converts a mixture of solution to a powder by spraying the solution to small droplet from and contract with the hot air. The solution is rapidly dried and formed to the encapsulated powder of the core material. Encapsulated powder can increase the stability and shelf-life of the core material in spray-dried powder. Wall material could protect the core material in spray-dried powder from environment condition such as oxygen, heat and/or moisture. Glass transition temperature is very important physicochemical value to estimate the powder state and the stability of core material in spray-dried powder (Roos, 2015). Molecular movant in the powder increase significantly above Tg. Powder properties such as stickiness, caking, crystallization of sugar, flavor release, stability of functional compounds depend on Tg of powder (wall material). The glass transition of the powder has been observed using differential scanning calorimetry (DSC) (Rahman, 2007) However, the heat capacity of MD is so small that it is hard to measure Tg by DSC (Roos, 2015).

Ablette *et al.* (1993), Aravanitoyannis *et al.* (1993), Roos (2015), Busin *et al.* (1996) and Truong *et al.* (2004) investigated Tg of fructose. TheseTg values reported were ranged from 5 to 25°C. Avaltroni et al. (2004) investigated the effect of molecular weight distribution of MD on Tg and viscosity in aqueous solution. Goula and Adamopoulos (2008) studied effect of malotodextrin addition during spray drying of tomato pulp in dehumidified air and indicated their Tg values range from 100 to 243°C. Tgs of MD were higher than several sugars.

In this study, the measurement method of Tg for emulsified flavor spray-dried powder was proposed using aroma sensor. Above glass transition temperature, flavor release rate might increase at rubber state of powder. Aroma (flavor) concentration could be usually measured by gas chromatography. Aroma sensor is simple instrument and has been successful in monitoring the aroma concentration. By using aroma sensor, the rapid increment of flavor release from spray-dried powder was measured at the linear programmed temperature (ramping method). Wall materials were used MD (dextrose equivalent (DE)=19) and two mixtures of MD and Fructose (Fr), 80wt% MD and 20wt% Fr, and 60wt% MD and 40wt% Fr. MD is the most commonly used wall materials for spray drying in food industry. When Fr was added to MD, Tg of the mixture was controlled with the composition. The emulsified hexanol powders were formed with those wall materials by spray drying. The aim of this report is to evaluate the measurement method of Tg using aroma sensor.

2. Materials and Methods

2.1 Materials

Maltodextrin (DE=19) and Fr were used for spray drying as a wall of microcapsule. MD (DE=19) was gifted from Matsutani Chemical industry Co, Ltd. (Itami, Japan) The core of microcapsule was a flavor, hexanol from Wako Pure Chemical Industries, Ltd. (Osaka, Japan). Sodium caseinate was used an emulsifier from Mitsubishi-Chemical Foods Corp. (Tokyo, Japan). All other regents were used the regent grade from Wako Pure Chemical Industries, Ltd. (Osaka, Japan).

2.2 Preparation of spray-dried powder

The mixture flavor of hexanol (4wt%), benzaldehyde (4wt%), d-limonene (4wt%), ethyl laurate (4wt%), and isoamyl caprate (4wt%) and hexanol (4wt%) in middle chain triglyceride oil in the solid were used as the model flavors. Three solid systems were prepared: MD (DE=19), blendings of MD and Fr (mass ratio) 4:1 and 3:2. Solid content was 50 wt%. The emulsifier, sodium caseinate was 3 wt% in the solid. Hexanol in MCT oil was added to the carrier solution to produce hexanol mass ratio to the total solids of 0.2 to 1. An emulsion was prepared by homogenizing the mixture using a Polytron homogenizer (PT-10, Kinematica GA, Littau, Switzerland) at dial position 8 for 3 min. The emulsion was spray dried in an Ohkawara-L8 spray dryer (Ohkawara Kakouki Co., Ltd., Yokohama, Japan), equipped with a centrifugal atomizer. The operational conditions of the spray drying were air inlet temperature of 140°C, air outlet temperature of 90°C, and rotational speed of the atomizer of 10,000 rev/min, feed rate of 20 mL/min, and airflow rate of 110 kg/h.

2.3 Release of flavor from the flavor powder at the linear programmed temperature

One gram of the emulsified flavor powder was added in the glass vessel ($24^{d}\times45^{h}$, 12^{φ}). The rubber cap of this vessel had two needles (20G), which one was the air supply port and other was the air sammpling port. The air sampling needle was connected to the aroma sensor (COSMOS model XP-329, Osaka, Japan) with a poly-urethane tube ($60\times6^{\varphi}$) (PISCO, Okaya, Japan). This aroma sensor is indium oxide-based sensor to measure flavor concentration. The air containing the released flavor was succeed with the mini-pomp of aroma sensor. The released flavor concentration from the vessel was measured with an aroma sensor. The vessel was setted in the aluminum bock ($100^{w}\times78^{d}\times50^{h}$) on the plate heater (ND-1A, As One, Osaka, Japan). This plate heater was used to control the temperature of spray-dried powder with the linear increment rate (0.3, 0.5 and 1^{o}C/min). Powder temperature and the intensity of the aroma sensor were recored with the data logger (GRAPHTEC, midi LOGGER GL220, Kanagawa, Japan). The result shows the suddenly increasing of released

fragrance at transition temperature. The signal intensity of the aroma sensor was plotted with the powder temperature.

2.4 Estimation of glass transition temperature of spray-dried powder

Tg of amorphous mixtures could be estimated with several expressions. (Gordon and Taylor, 1952, Fox, 1956, Couchmann and Karasz, 1958)

Tg of spray-dried powders could be predicted by using Couchmann and Karasz equation (1978).

$$Tg = \frac{\sum_{i=1}^{n} w_i \Delta Cp_i Tg_i}{\sum_{i=1}^{n} w_i \Delta Cp_i} \quad (1)$$

where Tg is glass transition temperature of mixture (^{o}C), Tg_i is glass transition temperature of component i (^{o}C), ΔCp_i is the change in heat capacity of component i between glassy and rubbery states (J/(g·^{o}C) and w_i is mass fraction of component i.

Maltodextrin has many kinds of structure that need to use specific equation to determine variable value. Busin, Buisson and Bimbenet equation (1996) uses for calculation Tg of maltodextrin at different DE (2-100).

$$Tg = -1.4(DE) + 449.5$$

where Tg is glass transition temperature of MD (K) and DE is Dextrose Equivalent of maltodextrins for range of DE 2-100 (r=0.98).

ΔCp of MD can determine from following equation (Bouquerand, 2008).

$$\Delta Cp = 0.387 + \frac{90.8}{Mn}$$

where ΔCp is the specific heat capacity of the glass to rubber transition (J/(g·^{o}C)) and Mn is the average number molecular weight (g/mol).

Table 1 Glass transition temperature and the specific heat capacity of wall material. (Roos, 2015)

Wall Material	Tg_i (°C)	ΔC_{pi} (l/g°C)
MD (DE=19)	149.75	0.46
Fructose	5	0.83
Casein	144	5.58
Water	-139	1.94

2.5 Statistical analysis

The data for physical properties of spray-dried powders were analyzed statistically using Excel 2013, Microsoft office professional plus software. All measurements were done at least 3 replicates. The results are shown as the value of averages ± standard deviations. One-way analysis of variance (ANOVA) with post hoc Tukay (HSD) test was done to identify the significance differences (p<0.05) between data sets.

3. Results and Discussion

3.1 Characteristics of emulsified flavor spray-dried powder

Table 2 shows the physical properties of spray-dried powder such as reconstituted oil-droplet diameter, powder diameter, and moisture content. Oil-droplet diameter and powder diameter for three powders were about 1 and 50 μm. In the calculation of Tg, the moisture content was used as shown in Table 2.

Table 2 Physical properties of spray-dried powder

	MD	MD/Fr (80/20)	MD/Fr (40/40)
Oil droplet diameter (μm)	0.87±0.02	1.18±0.02	1.41±0.02
Powder diameter (μm)	55±3.7	57±2.4	40.8±2.3
Moisture content (wt%)	1.57±0.001	1.40±0.001	1.42±0.001
Flavor		Retention (%)	
Hexanol	102.6	72.4	68.2
Benzaldehyde	86.2	73.4	71.1
d-Limonene	95	101.8	104.1
Ethyl lauric acid	87.4	90.6	92.4
Ethyl hexanoate	94.6	90.8	90.4

3.2 Measurement of glass transition temperature, Tg of emulsified flavor powder

Apparent Tg was measured by flavor release measurement of spray-dried powder. Figure 1 shows the flavor release behaviors from emulsified flavor powder with MD (DE=19) for three linear increment rates of temperature (0.3, 0. 5 and 1ºC/min). The intensity of aroma sensor increased significantly at the specific temperature about 130ºC. At slow temperature increment rate, 0.3ºC/min, the intensity of aroma sensor increased gradually and rapidly increased at 131ºC. At 0.5 and 1.0ºC/min of the temperature increment rate, the aroma intensity was almost constant, near zero and rapidly increased at 131ºC.

Tg of Fr, glucose and sucrose were reported about 5, 31 and 62ºC. Fructose has very low glass transition temperature in the conventional sugars. When fructose was mixed MD, the mixture of fructose and MD might have lower Tg than that of MD (DE=19). To evaluate the measurement method of Tg using aroma sensor, the mixtures of Fr and MD (DE=19) were used 20wt% Fr and 80%MD, and 40wt% Fr and 60 wt% MD. Figure 2 and 3 show flavor release behaviors from emulsified flavor powder with those mixtures, 20wt% Fr and 80%MD, and 40wt% Fr and 60wt% MD.

As shown in Figs. 2 and 3, the addition of Fr to MD decreased the apparent Tg, which are the intercept temperature at the rapidly increase of aroma-sensor intensity. The apparent Tg were obtained about 116 and 70 ºC, respectively for 20wt% Fr and 80%MD, and 40wt% Fr and 60 wt% MD. Tg of the powder (40wt% Fr and 60 wt% MD) was 70ºC for spray-dried powder containing hexanol in MCT oil. For spray-dried powder containing flavor mixture, Tg values were 130, 110, and 72ºC, respectively. This experimental Tg was lower than the calculated value. However, Tg values for MD and MD/Fr (80/20) were similar values by the calculated Tg.

These data indicated that the apparent Tg could be estimated with the specific temperature of rapid increase of flavor release rate at the linear programmed temperature by aroma sensor.

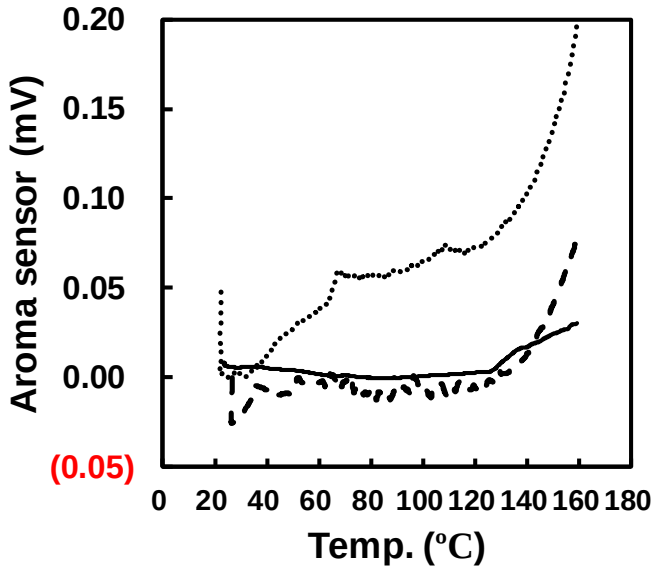

Figure 1 Flavor release behaviors from emulsified flavor powder with MD(DE=19). Temperature increment rate was 0.3ºC/min, thin dotted line; 0.5ºC/min, thick dotted; and 1ºC/min, solid line.

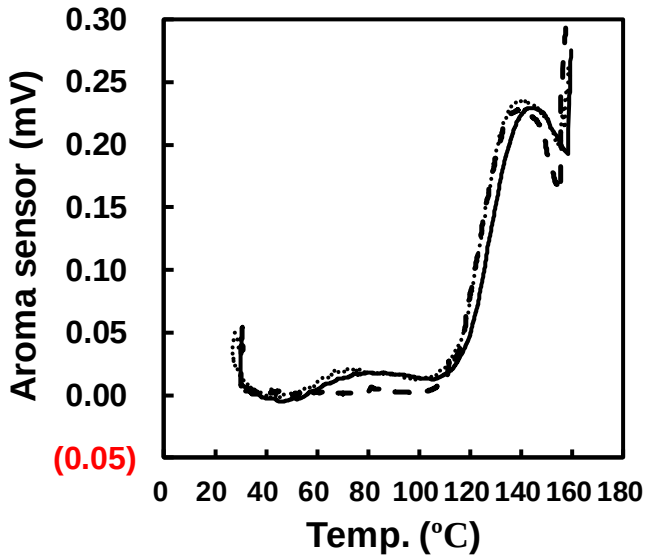

Figure 2 Flavor release behaviors from emulsified flavor powder with 20wt% Fr and 80wt% MD. Lines are same temperature increment rates as Figure 1.

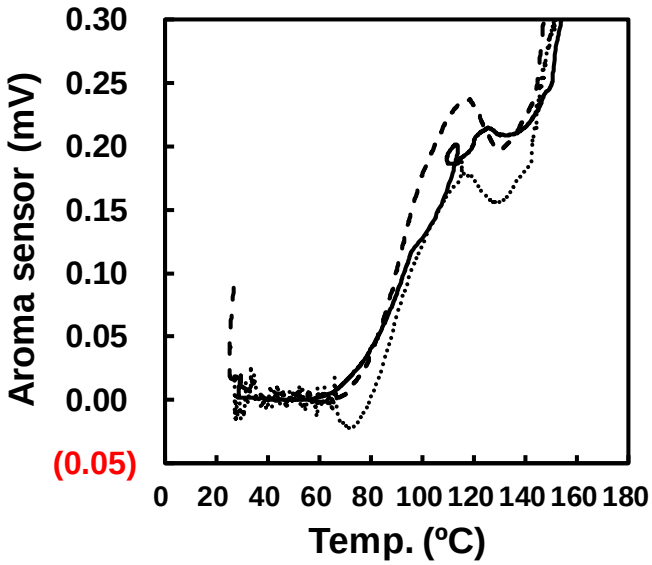

Figure 3 Flavor release behaviors from emulsified flavor powder with 40wt% Fr and 60wt% MD. Lines are same temperature increment rates as Figure 1.

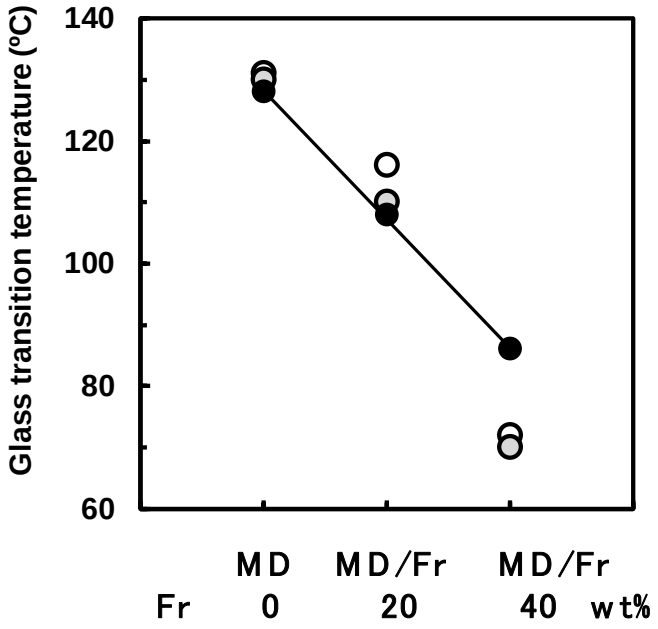

Figure 4 Comparison of Tg from the experimental value using aroma sensor and the calculated value by Couchmann and Karasz equation. ●, Calculated value; ○, Flavor mixture; ●, hexanol in MCT oil

4. Conclusion

By using aroma sensor, apparent Tg could be estimated using the rapid increment temperature of hexanol release from the emulsified flavor powder at the linear programmed temperature. Tg values for MD (DE=19), MD/Fr (80/20) and MD/Fr (60/40) were obtained about 131, 116, and 70ºC, respectively in this experiment. These Tgs were similar the calculated values by Couchmann and Karasz equation.

Acknowledgements

My thanks to JASSO scholarship supported scholarship for study in Japan. The substances and equipment supported from food engineering laboratory, Kagawa University, Japan.

References

Avaltroni, F. 2004. Maltodextrin molecular weight distribution influence on the glass transition temperature and viscosity in aqueous solutions. Carbohydrate Polymers. 58:323–334.

Bhandari, B.R. 1999. Implication of glass transition for the drying and stability of dried foods. Journal of Food Engineering. 40:71–79.

Busin, L., Buisson, P. and Bimbenet, J.J. 1996. Notion de transition vitreuse appliqué au séchage par pulverisation de solutions glucidiques. Sciences Des Aliments. 16(5):443–459.

Couchman, P.R. and Karasz, F.E. 1978. A classical thermodynamic discussion of the effect of composition on glass-transition temperatures. Macromolecules. 11(1):117–119.

Gharsallaoui, A. 2007. Applications of spray-drying in microencapsulation of food ingredients: An overview, Food Research International. 40(9):1107–1121.

Kanan, S.M., El-Kadri, O.M., Abu-Yousef, I.A. and Kanan, M.C. 2009. Semiconducting Metal Oxide Based Sensors for Selective Gas Pollutant Detection. Sensors.

Liu, Y. 2006. Glass Transition and Enthalpy Relaxation of Amorphous Food Saccharides. Journal of Agricultural and Food Chemistry. 54(16):5701–5717.

Pierre, E. 2008. Bouquerand, Moisture Stability of Maltodextrin-Based Delivery Systems. Food Biophysics. 3(2):182–185.

Rahman, M.S. 2007. Measurement of glass transition temperature by mechanical (DMTA), thermal (DSC and MDSC), water diffusion and density methods: A comparison study. Chemical Physics Letters. 440(4–6):372–377.

Roos, Y.H. and Drusch, S. 2015. Phase Transitions in Foods (2nd ed.). Nikki Levy, USA.

Slade, L. 1995. Water and the Glass Transition - Dependence of the Glass Transition on Composition and Chemical Structure: Special Implications for Flour Functionality in Cookie Baking. Journal of Food Engineering. 24:431–509.

Xu, P., Cheng, Z. Pan, Q., Xu, J., Xiang, Q., Yu, W. and Chu, Y. 2008. High aspect ratio In2O3 nanowires:Synthesis, mechanism and NO2 gas-sensing properties. Sensors and Actuators B. 130:802–808.