A simple and cheap method for estimating the glass transition temperature ($T_g$) of powders was proposed. This involved measuring the discoloration process of a dye added to the powders under temperature-programmed heating conditions. The method was applied to evaluate the $T_g$ values of mixtures of maltodextrin and fructose, containing betanin, a natural dye. The $T_g$ values obtained by this method almost agreed with those calculated by the Couchman and Karasz equation using the $T_g$ values for constituents in the mixture, thus indicating the validity of the method.

Keywords: glass transition temperature, betanin, discoloration

1. Introduction

In many cases, ingredients like carbohydrates, lipids, and proteins exist in a disordered structure, i.e., an amorphous state, in foods with low moisture content [1,2]. This amorphous state is further categorized into glassy and rubbery states [3]. Movement and diffusion of molecules are more remarkably restricted in the glassy state than in the rubbery one [4]. The transition between the glassy and rubbery states is called glass transition, and the temperature at which this transition occurs is the glass transition temperature ($T_g$) [1]. The glass transition from the glassy state to rubbery one occurs as temperature increases. An increase in moisture content lowers the glass transition temperature [3]. Since glass transition enhances the mobility of molecules, it promotes chemical and physical changes [3,5].

Preservability of food is higher in the glassy state than in the rubbery one, and food quality remains high in the glassy state. Therefore, understanding of glass transition plays an important role in reasonably determining food preservation conditions [4]. For example, the following phenomena occur in the rubbery state: acceleration of non-enzymatic browning reactions [6], easy release of flavor from powders [1,3,7], increased permeability of oxygen and subsequent promotion of lipid oxidation in encapsulated lipids due to relaxation of the matrix structure [1,3,8,9], reduction in crispness and flowability, increase in stickiness for powders and snacks [1,10,11], and facilitated blooming due to crystallization of sugars in chocolate [12].

Differential scanning calorimetry and thermal mechanical analysis are commonly used for measuring $T_g$ [1,4,5]. Nuclear magnetic resonance, electron spin resonance, and dielectric relaxation are also used for this purpose [1,4,13]. Equipment for these measurements is generally expensive, and pretreatment is necessary for some measurements.

In this study, we focused on the fact that reaction velocity changes significantly at the glass transition temperature, and also on a method for estimating the $T_g$ from the discoloration of a dye under temperature-programmed heating conditions.

2. Materials and Methods

2.1 Materials

Maltodextrin of dextrose equivalent=19, which is abbreviated as MD, was obtained from Matsutani Chemical Industry (Itami, Japan). Betanin (4-((2-(2-carboxy-5-(β-D-glucopyranosyloxy)-2,3-dihydro-6-hydroxy-1H-indol-1-yl)ethenyl)-2,3-dihydro-(S-(R',R'))-2,6-pyrindinedicarboxylic acid), which

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had been dispersed in dextrin powders by the manufacturer, and fructose were purchased from Wako Pure Chemical Industries (Osaka, Japan). The content of betanin and the dextrose equivalent of the dextrin powders in the commercial preparation had been roughly estimated to be 0.16% (w/w) and 32, respectively [14].

2.2 Preparation of maltodextrin-based powers containing betanin

The MD-based powders containing betanin were prepared by spray drying. Table 1 shows the composition of the feed solutions for preparing the powders. The solid contents of all the solutions were 50% (w/w). A feed solution was fed into a B-290 Mini spray-dryer (Büchi, Flawil, Switzerland) through a centrifugal atomizer at a flow rate of 20 mL/min. The air temperatures at the inlet and the outlet were 120°C and 73–76°C, respectively. The flow rate of air was ca. 0.9 m³/min. The powders prepared were collected in a cyclone.

As shown in Table 1, for the powders prepared from the mixtures of MD and fructose the fructose contents were 20% and 40% (w/w), and the powders are referred to as MD+20%Fru and MD+40%Fru, respectively. The powders containing no fructose are called MD-alone.

2.3 Discoloration of betanin in the powders

The betanin-containing powders (0.1 g) were weighed into a test-tube with a screw cap. Nineteen tubes were prepared for each sample. The tubes were placed in an aluminum block and heated on a programmable hot plate (ND-1A, As One, Osaka, Japan) from 30°C to 260°C, at a temperature-raising rate of 1.0, 0.5 or 0.3°C/min. The temperature in the tube was recorded using a TR-V550 data logger (Keyence, Osaka, Japan). A tube was removed from the aluminum block at regular intervals and immediately immersed in ice-water to cool to room temperature. 5 mL of water was added to the tube to dissolve the powders. The fraction of remaining betanin was evaluated from the absorbance of the solution at 530 nm, which was measured using a V-560 spectrophotometer (Jasco, Hachioji, Japan) at room temperature. The fraction, Y, was defined as the ratio of the absorbance of the solution at any time to the solution at time=0 min.

2.4 Moisture content of the powders

About 2 g of powder was precisely weighed and bone-dried using an HB43 moisture analyzer (Mettler-Toledo, Tokyo, Japan) at 160°C. The sample weight reached a constant value after about 10 min. The moisture content was calculated from the difference in weight before and after drying. The moisture content was measured in triplicate, and the mean value was reported along with the standard deviation.

3. Results and Discussion

3.1 Discoloration of betanin at different temperature-raising rates

Figure 1 shows the fractions of betanin in MD-alone, MD+20%Fru, and MD+40%Fru powders during temperature-raising at 0.5°C/min. The betanin in the MD-alone was discolored more slowly than those in the MD+20%Fru and MD+40%Fru powders. For all the samples, betanin scarcely discolored at temperatures as low as 80°C. Above that temperature, betanin gradually discolored and the discoloration accelerated with increasing temperature. Discoloration of betanin in the MD+40%Fru was a little faster than that in the MD+20%Fru powders.

Figures 2(a), (b), and (c) illustrate the changes in the fraction of remaining betanin in the MD-alone, MD+20%Fru, and MD+40%Fru powders respectively, at the

![Fraction of remaining betanin vs. Temperature](image-url)

Table 1  Compositions of the feed solutions to prepare maltodextrin-based powders containing betanin.

| Sample      | MD-alone | MD+20%Fru | MD+40%Fru |
|-------------|----------|-----------|-----------|
| Maltodextrin [g] | 96       | 38.4      | 57.6      |
| Fructose [g]  | 0        | 9.6       | 38.4      |
| Betanin* [g]  | 4        | 2         | 4         |
| Water [g]     | 100      | 50        | 100       |

*dispersed in dextrin powders at the content of ca. 0.16% (w/w).
different temperature-raising rates. The discoloration of betanin depended slightly on the temperature-raising rate, and the change in the remaining betanin content with increasing temperature seemed a little faster at lower temperature-raising rate, although not markedly.

### 3.2 Estimation of glass transition temperature of maltodextrin–fructose mixture

As shown in Fig. 2, the discoloration of betanin in all the powders seemed accelerated at 70 to 100°C. However, from Fig. 2, it would not be easy to estimate the temperature at which the discoloration became noticeable. Discoloration of betanin obeys first order kinetics [15]. Assuming that the temperature dependence of the rate constant is given by the Arrhenius equation, the fraction of remaining betanin, $Y$, is related to the absolute temperature at the temperature-raising rate, $\alpha$, by the following equation [16]:

$$\ln \left( -\frac{\alpha \ln Y}{RT^2} \right) = -\frac{E}{RT} + \ln \left( \frac{A_0}{E} \right) \quad (1)$$

where $R$ is the gas constant, $E$ is the activation energy, and $A_0$ is the frequency factor.

Figure 3 shows the plots of the left side of Eq. (1) against $1/T$ for the discoloration of betanin in powders with different fructose contents. Irrespective of the value of $\alpha$, the plots should, in principle, lie on a single line for each powder, but the values plotted did somewhat depend on the $\alpha$. However, in any case, the plots were represented by two straight lines: one down to the right and the other almost parallel to the horizontal axis. At temperatures lower than $T_g$, the powders are in the glassy state, and the betanin hardly discolors. On the other hand, when the temperature is higher than $T_g$, the powders are in the rubbery state, and betanin discoloration is considered to progresses. Based on this speculation, $T_g$ was obtained from the intersection of the two lines. Figure 4 shows that for powders with different
fructose contents, the estimated $T_g$ value ranged from 70 to 100°C. Although the powders had somewhat different moisture contents, there was the obvious tendency that the $T_g$ decreased at higher fructose contents.

### 3.3 Activation energy for discoloration of betanin in powders

According to Eq. (1), $E$ and $A_0$ associated with the discoloration of betanin at each temperature-raising rate were calculated from the slope and intercept of the straight line at temperatures higher than the $T_g$. The $E$ and $A_0$ values estimated at the three temperature-raising rates were averaged and plotted against the fructose content of the powders (Fig. 5). Both the $E$ and $A_0$ values were larger for the powders with higher fructose content.

The $E$ values were plotted against the $A_0$ values on a semi-logarithmic scale in the inset of Fig. 5. The plotted values lie on a straight line expressed by the following equation:

$$E = RT_\beta \ln A_0 + \gamma$$

This equation is one of the expressions describing the enthalpy-entropy compensation \([17,18]\); $T_\beta$ is a parameter called the isokinetic temperature and $\gamma$ is a constant. The $T_\beta$ value was evaluated to be 289 K (16°C) from the slope of the line. The fact that the compensation held indicates that coexistence of fructose does not affect the mechanism of betanin discoloration.

### 3.4 Comparison of the estimated glass transition temperature with the calculated temperature

The validity of the proposed method was examined by comparing the $T_g$ values obtained in this method, $T_{g,exp}$, with those estimated by the Couchman and Karasz equation, $T_{g,cal}$ \([19]\):

$$T_{g,cal} = \frac{\sum w_i \Delta c_{p,i} T_{g,i}}{\sum w_i \Delta c_{p,i}}$$

where $T_{g,i}$ is the glass transition temperature of component $i$ ($i$=maltodextrin, fructose and water), $\Delta c_{p,i}$ is the change in heat capacity of component $i$ between glassy and rubbery states, $w_i$ is the mass of component $i$ in the mixture. It has been indicated that the $T_g$ estimated by the equation does not always coincide with the measured one \([20]\). However, the equation was used to estimate the $T_g$ as an indicator with some reliability since the system investigated here is a simple mixture of MD and fructose.

The $T_{g,i}$ and $\Delta c_{p,i}$ values of maltodextrin were estimated by Eqs. (4) and (5), respectively \([21,22]\):

$$T_{g,i} = -1.4DE + 176.4$$

$$\Delta c_{p,i} = 0.387 + 90.8/M_n$$

where $M_n$ is the number-averaged molecular mass of maltodextrin, calculated from the DE value and molecular mass of glucose residue. The $T_{g,i}$ and $\Delta c_{p,i}$ values of fructose and water were cited from literature. The $T_{g,i}$ and $\Delta c_{p,i}$ values of the components are summarized in Table 2. The $T_{g,cal}$ values of MD-alone, MD+20%Fru, and MD+40%Fru powders were calculated using Eq. (3) using the $T_{g,i}$ and $\Delta c_{p,i}$ values, and the relationship between the $T_{g,cal}$ and $T_{g,exp}$ values is shown in the inset.
of Fig. 4. The betanin used was dispersed in dextrin powders of DE=32. The influence of the dextrin on the \( T_{g,cal} \) is estimated to be 0.5°C at the maximum and it would be insignificant. Since the weight fraction of betanin in the powders was only 6.4 \( \times 10^{-5} \), the effect of the betanin itself on the \( T_g \) should be negligibly small. Although there is a slight deviation, the values plotted are almost on a diagonal line, indicating the validity of the simple and cheap method proposed here to estimate the glass transition temperature of a powdery material.

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和文要約

定速昇温過程におけるベタニンの退色に基づく
粉体のガラス転移温度の推定法

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含水率の低い食品中の成分は多くの場合、無秩序な構造（非晶質）で存在し[1,2]。その構造はガラス状態およびラバー状態に分類される[3]。ガラス状態では分子の動きが大きく制限される[4]。ガラス状態とラバー状態の変化をガラス転移といい、転移が起こる温度をガラス転移温度 \( T_g \) という[1]。温度や含水率が高くなると、ガラス状態からラバー状態に転移する[3]。このガラス転移は分子の運動性を高めるので、化学的変化や物理的変化を促進する[3,5]。

ガラス状態にある食品は保存性が高く品質が保持されるので、食品の保存条件を合理的に決定するうえで、ガラス転移の理解は大変である[4]。差分走査熱量分析（DSC）や熱機械分析が \( T_g \) の測定に汎用される[1,4,5]。また、核磁気共鳴、電子スピン共鳴や誘電緩和も利用される[1,4,13]。しかし、これらの測定に用いる器機は高価であり、また前処理が必要な場合もある。

ベタニンは、室温よりやや高温で一次反応速度式に従って退色する天然色素である[14]。本研究では、温度を一定の速度で上昇させた定速昇温条件下で、粉体に添加したベタニンの退色を汎用的な熱機械分析（DSC）によって測定した。粉末を昇温速度 \( R \) の内図（Fig. 2）と温度 \( T \) の関係は式（1）に従った。

\[
\ln \left( \frac{\alpha \ln Y}{R^2T^2} \right) = \ln \left( \frac{A_0}{E} \right) - \frac{E}{R} + \ln \left( \frac{A_0}{E} \right)
\]

ここで、\( \alpha \) は昇温速度、\( R \) は気体定数、\( E \) は活性化エネルギー、\( A_0 \) は頻度因子である。種々の粉体に対する式（1）のプロット（Fig. 3）は、いずれの粉体についても高温側と低温側の2本の直線で表され、その交点からそれぞれの粉体の \( T_g \) を算出した。フルクトースの含有率が高くなると \( T_g \) が低下した（Fig. 4）。また、式（1）より求めた \( E \) と \( A_0 \) をともにフルクトース含有率が高くなると大きくなくなった（Fig. 5）。さらに、\( E \) と \( A_0 \) の対数値のプロットは直線となり（Fig. 5の内側）、粉末中でのベタニンの退色に対して熱力学的補償効果[16,17]が成立した。したがって、フルクトースの存在はベタニンの退色反応に影響を及ぼさない。

提案法により求めた \( T_g \) の妥当性は、汎用的なDSCなどにより測定した \( T_g \) との比較により検証するのが一般的である。しかし、ここでは高価な装置を用いないことを前提としているので、以下の方法で妥当性を検討した。それぞれの粉体の組成 \( w_i \) と \( T_g \) との関係[19-22]、Couchman–Karasz式[18]により、ガラス転移温度 \( T_{g,cal} \) を求め、提案法により \( T_{g,exp} \) と比較した（Fig. 4の内側）。両者はほぼ一致し、簡便な提案法の妥当性を支持した。

このように、粉体に色素であるベタニンを添加し、定速昇温条件下における色素の退色から、高価な装置を用いることなく、粉体の \( T_g \) が簡便に求められることを示した。