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RESEARCH NOTE

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Estimating the Glass Transition of Oligosaccharides Mixtures through the State Diagram

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Abstract State diagram of highly concentrated branched oligosaccharides (HBOS) was constructed to better understand phase behavior of mixtures with different size of oligosaccharides. It showed dramatic plasticizing effect on glass transition, which was successfully described based on Couchman-Karasz equation model. T_g' estimated from state diagram corresponded well with previous empirical data measured by maximum ice formation through isothermal holding (annealing) process. Estimated T_g' and C_g' values were -36.3°C and 79.99%, respectively. T_g' value of HBOS was approximately 10°C higher than that of sucrose, while C_g' value was similar to those of general carbohydrate materials, which could be useful for applications in frozen system.

Keywords: Highly concentrated branched oligosaccharides, glass transition, Couchman-Karasz equation

Introduction

Investigation of the phase behavior of carbohydrates is a valuable base for estimating and understanding the stability of frozen and freeze-dried food products and pharmaceuticals. The glass transition has been widely used as a major impact parameter for the stability estimation, while most of the reports were focused on a single component with water as a plasticizer and were interpreted for realistic systems. The Couchman-Karasz equation has been applied to predict the glass transition phenomenon in polymer science and was extended to the biopolymer systems including small carbohydrates and macromolecules (1-7).

Oligosaccharides are extensively used in the food industry, particularly for food formulations, due to their unique physical and physiological properties. Through enzymatic reactions, we developed branched oligosaccharides, which were successfully applied to cryoprotect the proteins in surimi, freeze-dried beef protein, and retard starch retrogradation (8-12). Although we previously revealed the mechanism of protein cryoprotection, a more logistic interpretation is possible using a state diagram. Here, we report a simple approach to establish a state diagram of oligosaccharide mixtures and compare it with the previous experimental data to confirm its applicability.

Materials and Methods

Preparation of highly concentrated branched oligosaccharides (HBOS) HBOS were prepared according to the previously described methods (8-12). The oligosaccharide mixtures were synthesized through enzymatic reactions, followed by yeast fermentation to remove fermentable sugars, mainly glucose and maltose. The resultant HBOS had a dextrose equivalent (DE) value of about 33 and the yield of 40% (w/w) (10). The sugar composition was determined by a High performance ion chromatography (HPIC) system according to a previous method (8).

Differential Scanning Calorimetry (DSC) DSC analyses were performed using a DSC 120 (Seiko Instrument Inc., Japan) equipped with an intracooler system using liquid nitrogen. The instrument was calibrated for heat flow using indium (ΔH, 334 J/g) and for temperature using indium (m.p., 156.6°C) and water (m.p., 0°C).

Preparation of samples Amorphous HBOS was prepared by freeze-drying 20% HBOS solution known to produce an amorphous state (13, 14). The freeze-dried materials were further dehydrated to 'zero' moisture content in a vacuum desiccator over P_2O_5 for 2 weeks to study the thermal behavior of anhydrous HBOS. This anhydrous HBOS was then rehumidified over saturated salt solutions for 48 hr to obtain samples of low moisture content (15, 16). The salt solutions used were LiBr, $LiCl \cdot H_2O$, $MgCl_2 \cdot 6H_2O$, and $NaBr \cdot H_2O$ with corresponding relative humidity values of 7, 11, 32, and 58 %. In addition, to determine their thermal phenomena at low temperatures, HBOS solutions of 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 60, and 79% (w/w) were prepared by weighing respective amounts of HBOS. They were then dissolved in water with mild heating at concentrations above 60%, until clear solutions were obtained (16).

Prediction of glass transition temperature The Couchman and Karasz equation, generally used to predict water plasticization of food components and materials, including carbohydrates and proteins, was used for the prediction of glass transition temperature in this study (1-3, 5).

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$$T_g=\frac{w_1T_{g1}+kw_2T_{g2}}{w_1+kw_2}$$

where T_g, T_{g1}, and T_{g2} are glass transition temperatures of the mixture (K), component 1 (HBOS), and component 2 (water, 135 K), and w_1 and w_2 are weight fractions of components 1 and 2, respectively, and k is the constant. This equation was used to calculate the T_g line of HBOS to establish the state diagram using experimental and predicted values. The T_g value of water (17) used was -138 °C. The value for the constant k was obtained based on the ratio of ΔC_p of water and HBOS ($\Delta C_{p2}/\Delta C_{p1}$).

Results and Discussion

The T_g value at low water content is important to the stability and control of crystallization in amorphous materials (14, 18). The T_g of the anhydrous amorphous HBOS was determined as 81.3°C, and it was drastically decreased by the plasticization of water (Fig. 1). T_g greatly decreased with small amounts of water with no relaxation endotherms by ice-melting during rewarming (data was not shown), which implies that the prepared samples were completely amorphous.

The changes in the apparent specific heat (ΔC_p) for amorphous HBOS at T_g was determined as 0.56 J/g · °C, which is lower than that of sucrose (0.6 and 0.77 J/g · °C) (16, 19). This phenomenon followed the general trend that ΔC_p is inversely proportional to the molecular weight. In addition, water played the role of a low molecular weight plasticizer; thus, a higher ΔC_p value was obtained for HBOS solutions than for the anhydrous HBOS sample.

A state diagram of HBOS was established based on the T_g and ΔC_p values (Fig. 1). Couchman (1) and Couchman and Karasz (2) reported that the k values in the equation is equivalent to $k=\Delta C_{p2}/\Delta C_{p1}$. The ΔC_p value of water was reported to be 1.94 (17), and from this value the empirical k value was calculated as 4.76 (±0.346). The T_g line drawn from the predicted values of Couchman-Karasz equation showed a good correlation with the experimental T_g values. The Couchman-Karasz theory is potentially the most useful in calorimetric investigations, because all the required physical parameters can be determined using DSC (4). This approach has been applied to malto-oligosaccharide (4), amylopectin-sugar (3) mixture, and tertiary mixtures of water-amylopectin-casein (5) as well. T_g' and C_g' values calculated from the state diagram were -36.3°C and 79.99%, respectively. T_g' correlated well with the measurement (-37.1°C) obtained through the isothermal holding process (9) and the measured value from a concentrated 79% (w/w) solution (Fig. 2). Compared to sucrose, T_g' was 10°C higher (16), while C_g' showed a similar value to the general carbohydrate materials (18).

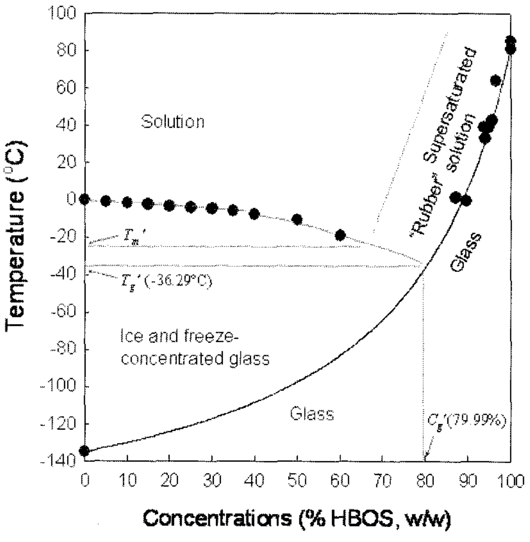

Fig. 1. A state diagram of HBOS.

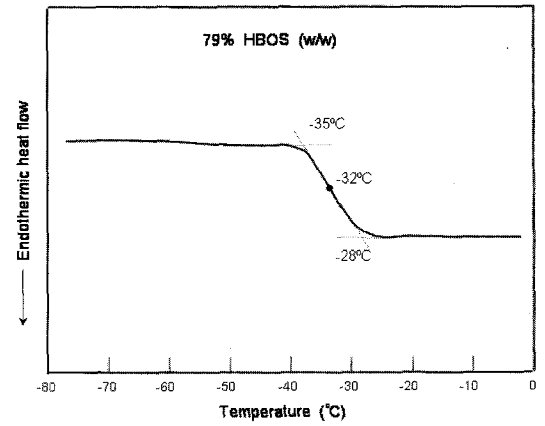

Fig. 2. DSC thermogram of 79% HBOS solution showing a distinct glass transition.

The state diagram describes the nonequilibrium nature of amorphous foods, as well as temperature and water effects on the physical properties of food. Thus, it can be applied to the changes caused by dehydration, crystallization, and freezing of foods (20, 21). In the case of freezing and frozen storage, glass transition temperature can be used as a probe to control the stability (22-26). Most foods have T_g values well below the freezing point, which increase with freezing process by freeze-concentration. Because the stability of frozen foods is related to the temperature difference between storage and T_g', it can be stabilized below T_g' and rapidly destabilized above T_g'. Thus, the resulting changes in the physical state can be estimated from state diagrams.

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