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FACULTAD DE CIENCIAS QUÍMICAS

PROGRAMA DE POSGRADO EN CIENCIAS EN BIOPROCESOS

EFECTO CRIOPROTECTOR Y COADYUVANTE DE LA MALTODEXTRINA EN LOS DIAGRAMAS DE ESTADO DE SISTEMAS RICOS EN AZÚCARES

ARTÍCULO DE INVESTIGACIÓN PARA OBTENER EL GRADO DE

DOCTOR EN CIENCIAS EN BIOPROCESOS

PRESENTA:

M.C. FLORES RAMÍREZ ALMA DE JESÚS

DIRECTOR DE TESIS

DR. MIGUEL ANGEL RUIZ CABRERA

SAN LUIS POTOSÍ, S.L.P. **DICIEMBRE DE 2021**

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FACULTAD DE
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San Luis potosí, Noviembre/30/2021

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Programa de Posgrado en Ciencias en Bioprocesos
Facultad de Ciencias Químicas
Universidad Autónoma de San Luis Potosí

Con atención a la Dra. Ruth Elena Soria Guerra
Coordinadora del Programa de Posgrado en Ciencias en Bioprocesos
FCQ-UASLP
Presente

Por medio de la presente hacemos de su conocimiento que la tesis llevada a cabo por la **M.C Alma de Jesús Flores Ramírez, titulada "Efecto crioprotector y coadyuvante de la maltodextrina sobre los diagramas de estado de sistemas ricos en azúcares"**, ha sido concluida y aprobada por el comité tutorial para dar inicio a los trámites correspondientes para su titulación, el cual tendrá lugar el día 14 de diciembre a las 11:00 horas en el Auditorio G203 de la Facultad de Ciencias Químicas.

ATENTAMENTE

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www.uaslp.mx

Av. Dr. Manuel Nava Núm. 6
Zona Universitaria • CP 78210
San Luis Potosí, S.L.P.
tel. (444) 826 24 40 al 46
fax (444) 826 2372

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RESUMEN EN EXTENSO 1

Freeze-Concentrated Phase and State Transition Temperatures of Mixtures of Low and High Molecular Weight Cryoprotectants

INTRODUCCIÓN

La congelación y el almacenamiento en congelado se utilizan ampliamente para la conservación a largo plazo de los alimentos. Durante la congelación, la temperatura de los alimentos se disminuye para promover la formación total o parcial de los cristales de hielo, reduciendo la disponibilidad de la disponibilidad del agua así como el crecimiento microbiano y la actividad enzimática (James & James, 2014). Sin embargo, la migración de la humedad y la recristalización del hielo, inducen daños celulares y/o estructurales en los alimentos. Estos daños estructurales generalmente se manifiestan con la liberación de líquidos intracelulares, cambios en la textura y pérdida por goteo (Berk, 2009). Es importante remarcar que la intensidad del daño de la congelación depende de la composición y estructura biológica del alimento. Otro de los parámetros a consideran durante la congelación es la velocidad de congelación es la que determina el tipo, tamaño y distribución del hielo en la matriz alimenticia. Como regla general se tiene establecido que velocidades bajas de enfriamiento tienden a producir cristales grandes de hielo extracelulares mientras que la congelación rápida genera pequeños cristales de hielo uniformemente distribuidos dentro y fuera de la célula. Sin embargo, el efecto benéfico de la congelación rápida en la calidad de alimentos sigue siendo un punto de controversia porque ha sido encontrado que, aunque estos hayan sido adecuadamente congelados mediante congelación rápida, los fenómenos de recristalización durante el almacenamiento siguen presentándose. Lo anterior es debido a que no toda el agua presente en el alimento está debidamente congelada a la temperatura estándar de -18°C (Nesvadba, 2008). Por ello, es necesario el control de la temperatura de almacenamiento a lo largo de la cadena de frio. La calidad de los alimentos

congelados se ve afectada por la temperatura de almacenamiento y el estado físico de la fase descongelada (Charoenrein &Harnkarnsujarit, 2017). Las temperaturas asociadas a la fracción máximamente crioconcentrada ($T_m´$ y T_g') se consideran como parámetros de referencia que determinan la estabilidad de los alimentos congelados, asumiendo que la formación máxima de hielo tiene lugar cuando los sistemas alimentarios se almacenan entre estas temperatura (Charoenrein & Harnkarnsujarit, 2017; Zaritsky, 2018) Por debajo de T_g', la matriz crio-concentrada alcanza el estado vítreo donde el movimiento molecular se hace extremadamente lento y cualquier cristalización de hielo se vuelve prácticamente imposible y por lo tanto se puede esperar estabilidad del alimento a largo plazo. Sin embargo, la mayoría de los alimentos tienen un valor de T_g' muy por debajo de la temperatura de congelación comercial (-18°C). En este contexto, el uso de crioprotectores de alto peso molecular, como la maltodextrina 4-7 DE, polidextrosa e hidrocoloides, para manipular el estado físico y elevar deliberadamente los valores de T_g' y T_m' de alimentos congelados por encima de la temperatura normal de almacenamiento de los congeladores comerciales puede ser una alternativa atractiva. Sin embargo protocolos de incorporación de compuestos crioprotectores a alimentos no han sido establecidos hasta el momento. Los factores de selección de estos solutos se han basado principalmente en su bajo costo, disponibilidad, características sensoriales agradables o aceptación en los alimentos, proceso de prueba y error así como de la experiencia de los fabricantes de alimentos. Por lo tanto se propone que la selección y rango de concentración del crioprotector sea en función de los valores T_g' y T_m'.

OBJETIVO

1. Determinar las temperaturas características de la matriz máximamente crioconcentrada (T_g', T_m') y el punto de congelación (T_m) de crioprotectores a diferentes concentraciones mediante DSC con la finalidad de establecer la concentración y tipo (s) de crioprotector.

MATERIAL Y MÉTODOS

Maltodextrina 4 DE (M), glucosa (G), y polidextrosa (P) grado reactivo fueron utilizadas como sustancias crioprotectoras, las cuales, fueron equilibradas sobre Drierite® con una actividad de agua (a_w) de 0 a temperatura ambiente por un periodo de 4 semanas. Las fracciones másicas X_M, X_G, X_P y X_W fueron establecidas usando un diseño experimental Distance-Based para mezclas de 4 componentes sujetos a las siguientes restricciones: $\sum_{i=1}^{n} X_i = 1 \; y \; 0.4 \leq \{X_W\} \leq 0.95$. Un total de 30 soluciones crioprotectoras fueron preparadas en viales de 1.5 ml mediante la adición directa de X_W para lograr un volumen de 1 ml. Alícuotas de 5-10 µl fueron tomadas de cada solución y fueron colocadas en charolas DSC (TA Instruments), las cuales fueron selladas herméticamente y se dejaron en equilibrio durante 7 días. Todos los análisis térmicos fueron realizados en un Calorímetro Diferencial de Barrido (DSC Q2000 (TA Instruments). Las muestras fueron sometidas a un método de escaneo convencional lineal el cual consistió en un enfriamiento a -70°C a una velocidad de 20°C/min, esta temperatura se mantuvo durante 3 min, y posteriormente fueron calentadas hasta 20°C a 10°C/min. Para muestras con una humedad de 40-60 % (b.h.) fue requerido un procedimiento de annealing a T_m'-1°C con el fin de maximizar la formación de hielo. Mientras que para muestras con X_M predominante, fue necesario someter las muestras a un calentamiento desde la temperatura ambiente hasta 80°C a 20°C/min para posteriormente continuar con el escanea lineal convencional, este procedimiento se realizó con la finalidad de lograr una completa homogenización de los componentes. Los valores de T_g' y T_m' fueron respectivamente asignados al punto medio del 1° y 2° paso de cambio de flujo de calor observados en los termogramas durante el calentamiento. La temperatura máxima correspondiente a la endoterma de fusión fue considerada como el punto de congelación (T_m). Un modelo cúbico de Scheffe fue usado para evaluar el efecto de la composición de las mezclas crioprotectoras $\{X_M, X_G, X_P\}$ disueltas en una fracción másica de agua (X_W) sobre las variables de respuesta (T_g', T_m' y T_m). Un análisis de

varianza (ANOVA) a un nivel de confianza de 95% ($p < 0,05$), el software Design-Expert® fue utilizado.

RESULTADOS

Los termogramas DSC de las soluciones crioprotectores revelaron la existencia de una transición vítrea para las soluciones de maltodextrina pura y dos transiciones para todas las demás soluciones. Las soluciones de maltodextrina pura mostraron valores más altos de Tg', Tm' y Tm (-6.3, 6.3 y 0.5°C) que los obtenidos para las soluciones congeladas de polidextrosa (-34.6, -22.6 y -7.3°C) y glucosa (-54.3, -38.2 y -15.6°C). Con el mismo contenido de humedad, esto se puede atribuir al mayor peso molecular de las maltodextrina DE 4. Estos resultados concuerdan con lo reportado en la literatura donde se han reportado que compuestos con alto peso molecular, presentan mayores valores de T_g' y T_m' .y T_m.

Se pudo observar en muestras ternaria acondicionadas a humedades de 40-95%, que el aumento de la concentración de las soluciones crioprotectores aumento la intensidad de las transiciones térmicas. En todos los contenidos de humedad, las mezclas ternarias exhiben transiciones globales bien definidas, indicando una buena compatibilidad de los crioprotectores.

Ningún aumento sinérgico de T_g', T_m' y T_m se encontraron cuando se analizaron mezclas de crioprotectores de alto y bajo peso molecular. Los valores más alto de T_g', T_m' y T_m' se encontraron para soluciones de maltodextrina al 40% de agua. Por otra parte, soluciones de glucosa 40% de agua presentaron los valores más bajos de T_g', T_m' y T_m'. Las soluciones crioprotectores restantes presentaron valores intermedios de acuerdo a lo que se ha publicado en literatura en relación a que las mezclas de biopolímeros compatibles exhiben temperaturas de transición de fase y estado intermedias por que los componentes de las mezclas actúan como plastificantes mutuos.

Los valores experimentales de T_g', T_m' y T_m' obtenidos y los modelos matemáticos propuestos en esta investigación pueden ser de gran ayuda para la formulación de medios crioprotectores que contienen más de dos componentes para

mejorar la estabilidad y calidad de almacenamiento de los alimentos congelados con contenido de humedad alto e intermedio y formulación modificables.

CONCLUSIÓN

Los valores de T_g', T_m' y T_m aumentan con el peso molecular del crioprotector. Además, el análisis estadístico de los datos ($p < 0.05$) demostró que tanto la composición del soluto como el agua deben considerarse en la formulación de medios crioprotectores, ya que se encontró que afectan significativamente los valores de T_g', T_m' y T_m ($p < 0,05$). Las expresiones matemáticas para T_g', T_m' y T_m en función de las fracciones de masa de los crioprotectores (X_M, X_G, X_P) y el agua (X_W) y sus interacciones se desarrollaron para guiar la formulación de medios crioprotectores que involucran mezclas de más de dos crioprotectores para mejorar la estabilidad en almacenamiento y la calidad de productos congelados con contenidos de humedad altos e intermedia.

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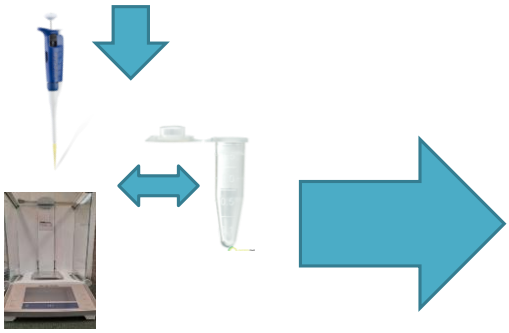
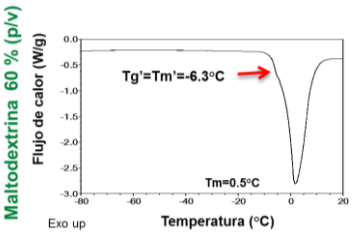
RESUMEN GRÁFICO 1



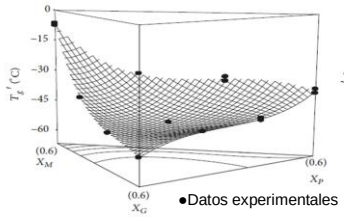
Preparación de soluciones crioprotectoras

Análisis calorimétrico

Caracterización térmica de soluciones crioprotectoras



Variación de T_g' en soluciones crioprotectoras



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Research Article

Freeze-Concentrated Phase and State Transition Temperatures of Mixtures of Low and High Molecular Weight Cryoprotectants

Alma J. Flores-Ramírez,[1] Pedro García-Coronado,[1] Alicia Grajales-Lagunes,[1] Raúl González García,[1] Miguel Abud Archila,[2] and Miguel A. Ruiz Cabrera[1]

[1]*Faculty of Chemical Science, University of San Luis Potosi, 6 Dr Manuel Nava Avenue, University Area, San Luis Potosí 78210, Mexico*
[2]*National Institute of Technology of Mexico, Technological Institute of Tuxtla Gutiérrez, Street Km 1080, Tuxtla Gutiérrez 29050, Mexico*

Correspondence should be addressed to Miguel A. Ruiz Cabrera; mruiz@uaslp.mx

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Although numerous studies have been conducted on the use of cryoprotectants to prevent the deterioration of food during freezing and frozen storage, scarce reports exist on the thermal transition properties of aqueous cryoprotectant solutions at frozen temperatures. The selection of a suitable cryoprotective medium for the long-term preservation of food requires knowledge of the effects of cryoprotectants and their concentration on the freeze-concentrated unfrozen phase and state transition temperatures known as T_g', T_m', and T_m. Calorimetric measurements were conducted to determine the T_g', T_m', and T_m values of thirty frozen aqueous solutions containing maltodextrin, polydextrose, and glucose, in which a distance-based experimental design was used for mixtures of four components to establish their corresponding mass fractions in the mixtures. Thermograms, measured during heating/rewarming from –70 to 20°C, were used to identify the glass transition and freezing temperatures. Mathematical expressions for T_g', T_m', and T_m as a function of the mass fractions of cryoprotectants and water and their interactions ($p < 0.05$) were developed to aid the formulation of cryoprotective media involving more than two cryoprotectants for adequate frozen conservation of high and intermediate moisture foodstuffs.

1. Introduction

Freezing and frozen storage are widely used for the long-term preservation of food. During freezing, the temperature of the food is lowered to promote the total or partial formation of ice crystals, reducing the availability of water and consequently the growth of microorganisms and enzymatic activity [1–4]. Frozen foods have an extended shelf-life of months compared to days or weeks for chilled or refrigerated foods [5, 6]. Additionally, frozen foods are preferred by consumers because freeze preservation ensures that the food products present better taste, texture, nutritional value, and freshness than those preserved by other methods such as dehydration, concentration, and pasteurization [2].

However, some negative changes in frozen foods caused by physical, chemical, and/or biochemical processes resulting from inadequate freezing rates or storage temperature need to be considered. The major physical change in frozen foods is moisture migration, which causes moisture loss by sublimation, moisture mobility and redistribution in food components, recrystallization of ice, and drip losses in thawed products [7]. It has also been noted that slow-freezing rates during freezing produce extracellular, large, sharp ice crystals, which cause water migration from the cells due to osmotic effects and subsequently lead to cellular dehydration and structural damage [3, 8–11]. On the other hand, among the various chemical changes that take place during freezing and frozen storage are lipid hydrolysis and oxidation, protein denaturation and oxidation, degradation of vitamins, and flavor changes [12].

To alleviate or moderate the deterioration of frozen foods, quick freezing involving the addition of cryoprotectants and phase/state transition concepts have been investigated [13–16]. Quick freezing rates promote the equilibrated formation

of small crystals inside and outside the products. Quick freezing, however, is only suitable for small samples and although fast freezing promotes the formation of small crystals inside the products, during frozen storage at the standard commercial freezing temperature of –18°C, ice crystals undergo metamorphic changes, thus reducing the advantages of fast freezing [1]. This phenomenon occurs because, at –18°C, foods exhibit an unfrozen phase in rubbery state, where mobility of unfrozen water may occur [17]. In addition, the small ice crystals formed under fast freezing conditions are thermodynamically unstable because of their high free energy, so they tend to combine with larger, more stable ice crystals during storage [2, 17]. Therefore, the stability and quality of frozen foods are significantly influenced by the storage temperature and physical state of the unfrozen phase [12, 18, 19].

The temperatures associated with the freeze-concentrated unfrozen phase (T_m' and T_g') are regarded as reference parameters determining the stability of frozen foods. It is assumed that maximum ice formation takes place when food systems are stored between these temperatures [12, 18–20]. It is also known that the unfrozen phase below T_g' leads to a glassy state with substantially increased viscosity (around 10^{10}–10^{12} Pa s), in which molecular motion becomes extremely low, and further crystallization of water into ice and chemical reactions associated with the molecular diffusion of water and other reactants are greatly reduced; therefore, long-term stability may be expected [13, 14, 17, 21–25]. However, the foods in this state are defined as nonequilibrium, metastable, amorphous, disordered materials exhibiting higher free volumes and energy levels than those of crystalline states. Therefore, some factors such as water sorption and temperature changes above T_g' will accelerate the molecular mobility related to chemical and physical changes in glassy frozen foods [12, 13, 19].

In the literature, it has been reported that T_m' and T_g' values exhibit slight variations with the water or solid content but, as a general trend, both parameters depend strongly on the type and molecular weight of the food components [20, 26–28]. Typically, it has been found that the T_m' and T_g' of homologous amorphous polymers such as maltodextrins decrease with the decreasing average molecular weight or increasing amount of plasticizer or moisture content [29–31]. For instance, T_g' values ranging from –15 to –43°C and T_m' values from –11 to –28°C have been reported for frozen solutions elaborated with 40% maltodextrin solutions with a dextrose equivalent (DE) ranging from 5 to 36 and respective molecular weights from 3600 to 500 Da [30].

However, fresh foods usually present high water contents and chemical compositions dominated by low molecular weight (LMW) components with T_m' and T_g' values well below the standard freezing temperature of –18°C. Thus, frozen storage between the T_m' and T_g' or below T_g' is sometimes impractical from an economic point of view [20, 32, 33]. In this context, the use of cryoprotectants with high molecular weight (HMW), such as maltodextrin 5 DE, polydextrose, and hydrocolloids, to manipulate the physical state and deliberately elevate the T_m' and T_g' of frozen foods to above the normal storage temperature of commercial freezers may be an attractive alternative [13, 34–36]. Another approach is the use of LMW cryoprotectants, such as dimethyl sulfoxide, glycerol, and glucose, to depress the freezing point (T_m) and thereby reduce the intracellular ice formation [11, 36–38]. It is important to note that a synergistic increase of T_g' was reported by Harnkarnsujarit et al. [39] for mixtures of LMW sugars (glucose and maltose) and phosphate salts such as Na_3PO_4, $Na_4P_2O_7$, $Na_5P_3O_{10}$, K_3PO_4, and $K_4P_2O_7$ as a result of intermolecular interactions between the components. However, literature reports on the resulting T_m' and T_g' values for aqueous frozen solutions containing mixtures of HMW and LMW cryoprotectants involving a large working range of water content for adequate frozen conservation of high and intermediate moisture foodstuffs, such as fruits, ice cream, purees, jams, etc., remain scarce.

On the other hand, the optimization and selection of cryoprotectants in food formulations are a challenging task because the choice of cryoprotectants is based largely on criteria such as low cost, availability, pleasant or acceptable sensory characteristics in foods, and trial-and-error processes and experience of the food manufacturers [15, 16, 40]. For instance, sucrose and sorbitol concentrations of 4–8% [15, 40], polydextrose concentrations of 1–10% [41, 42], glucose concentrations of 5-15% [43], maltodextrin concentrations of 5-35% [36, 44–46], and maltodextrin-sugars concentrations of 20% (glucose, fructose, and sucrose) [47] have been used as cryoprotectant additives. In some cases, it has been reported that low levels of sugars and sorbitol impart a sweet taste to the products [40, 41, 43]. On the other hand, maltodextrin and polydextrose are nonsweetening and have low viscosities at high solid contents with good solubility [34, 35]. It is evident that the selection of cryoprotectants and their concentration range need to be standardized based on the resulting T_m' and T_g' values rather than on other criteria previously mentioned.

Therefore, this study was based on the assumption that the selection of a cryoprotectant medium suitable for the long-term preservation of food requires knowledge of the effect of cryoprotectants and their concentration on the freeze-concentrated phase and state transition temperatures. The evaluation of the T_g', T_m', and T_m values of different frozen aqueous cryoprotectant solutions elaborated with pure or combined cryoprotectants using differential scanning calorimetry (DSC) involving a large range of water contents was the main focus of this study. For this purpose, thirty aqueous solutions containing maltodextrin, polydextrose, glucose, and their mixtures in a concentration range of 40–95% water were studied.

2. Materials and Methods

2.1. Preparation of Cryoprotectant Solutions. Analytical grade maltodextrin 4–7 DE (product no. 419672; molecular weight 3600), crystalline glucose (product no. G5767; molecular weight 180.16), both from Sigma-Aldrich CO. (St. Louis, MO), and commercial food grade noncrystalline polydextrose (molecular weight 342.3) from Henan Tailijie Biotech Co.

(China) were the employed cryoprotectants. Each cryoprotectant was previously equilibrated over Drierite® (anhydrous calcium sulfate, $a_w \approx 0$) in a desiccator at room temperature for several weeks in order to obtain completely dry samples. The moisture content of these equilibrated samples was then determined by the AOAC method [48] and taken into account for the preparation of solutions, as described below.

Cryoprotectant solutions were prepared gravimetrically by weighing the appropriate amount of solid material using a Mettler-Toledo microbalance (model AG245; RS232 interface; readability 0.1 mg/0.01 mg) and adding the appropriate volume of distilled water. A completely randomized distance-based experimental design for mixtures of four components was used to establish the mass fraction of maltodextrin (X_M), glucose (X_G), polydextrose (X_P), and water (X_W) in the cryoprotectant solutions. The Modde 7.0 (Umetric AB) statistical software was used for the experimental design, in which the constraints $\sum_1^n X_i = 1$ and $0.4 \leq X_W \leq 0.95$ were considered. Five replicate points were used and a total of 30 cryoprotectant solutions, including pure components as well as binary and ternary mixtures, were prepared (Table 1).

Solutions containing high proportions of maltodextrin were dissolved in Eppendorf safe-lock tubes placed in a water bath at a controlled temperature (40°C). In all cases, the solutions were well stirred to obtain clear solutions at room temperature and after stored at 4°C for several days to allow for equilibration of the moisture content throughout the sample [27, 33]. The solid content of the equilibrated cryoprotectant solutions was confirmed with a digital refractometer (AR 200, Leica) at room temperature.

2.2. Phase and State Transition Analysis of Frozen Cryoprotectant Solutions. DSC measurements were carried out using a Q2000 differential scanning calorimeter (TA Instruments, Delaware 19720, USA) with a RCS90 cooling system using ultrapure nitrogen as the purging gas at a flow rate of 50 mL/min.

Samples of the cryoprotectant solutions (approximately 5–10 mg) were weighed in aluminum pans, hermetically sealed, and then placed in the DSC instrument at room temperature; an empty pan was used as the reference. The calorimetric methodology proposed by Sablani et al. [20] and Ruiz-Cabrera et al. [33] was used for determination of the T_m, T_m', and T_g' values of the samples. Before starting the experiments, the samples were equilibrated in the DSC apparatus at 20°C for 2 min. The samples were then cooled to −70°C at 20°C/min to quickly reach the amorphous state, maintained at this temperature for 3 min, and then heated back to room temperature at a rate of 10°C/min. It is important to note that, for cryoprotectant solutions containing water in the range of 40% to 60% wet basis ($0.4 \leq X_W \leq 0.6$, Table 1), an annealing procedure at (T_m' − 1)°C for 30 min was implemented to obtain maximally freeze-concentrated cryoprotectant matrices [33, 49]. The apparent value of T_m' in each experiment was determined from the first thermal analysis in nonannealed state. In these cases, each cryoprotectant solution was cooled to −70°C, held for 3 min, heated at 10°C/min to the annealing temperature (T_m' − 1)°C, and then annealed for 30 min. Following annealing, the samples were cooled at 20°C/min to −70°C, held for 3 min, and then reheated at 10°C/min back to room temperature. The midpoint T_g' and T_m' values were determined using the half-height method from the first and second step changes of the heat flow, as observed in the DSC thermograms during the heating process [33, 50, 51]. In this study, the peak temperature corresponding to the melting endotherm was considered to be the freezing point (T_m). In all cases, the Universal Thermal Analysis software (version 4.4A) was used.

2.3. Statistical Analysis of the Data. Analysis of variance (ANOVA) was performed with a confidence level of 95% ($\alpha = 0.05$) using the Modde 7.0 statistical software (Umetrics, Kinnelon, NJ, USA). The Scheffe cubic model (Eq. (1)) with interactions was used to analyze the effect of the chemical composition of the cryoprotectant solutions (X_M, X_G, X_P, and X_W) on the response variables (T_g', T_m', and T_m) as follows:

$$\begin{aligned} Y = {} & a_0 X_M + a_1 X_G + a_2 X_P + a_3 X_W + a_4 X_M X_G + a_5 X_G X_P \\ & + a_6 X_P X_W + a_7 X_M X_W + a_8 X_G X_W + a_9 X_M X_P \\ & + a_{10} X_M X_G X_P + a_{11} X_M X_G X_W + a_{12} X_M X_P X_W \\ & + a_{13} X_G X_P X_W + a_{14} X_M X_G (X_M - X_G) \\ & + a_{15} X_M X_P (X_M - X_P) + a_{16} X_M X_W (X_M - X_W) \\ & + a_{17} X_G X_P (X_G - X_P) + a_{18} X_G X_W (X_G - X_W) \\ & + a_{19} X_P X_W (X_P - X_W) \end{aligned} \quad (1)$$

where a_0 to a_{19} are the regression coefficients of the model. A backward elimination regression with an α value of 0.10 was applied and hierarchical models were obtained from Eq. (1).

3. Results and Discussion

3.1. Determination of T_g', T_m', and T_m in Frozen Cryoprotectant Solutions. The DSC thermograms showing the process of rewarming from −70 to 20°C for annealed solutions of maltodextrin (Experiment 2), polydextrose (Experiment 1), and glucose (Experiment 27), all conditioned at 40% water, are shown in Figures 1(a)–1(c). No evidence of an exothermic peak associated with the recrystallization of unfrozen water is observed in the rewarming thermograms, confirming that maximally freeze-concentrated phases were obtained after the annealing treatment at T_m'-1°C for 30 min. Instead, the DSC thermograms show thermal events in which the endothermic peak of ice melting is the most visible feature, preceded by one or two changes in the baseline with characteristics typical of a glass transition depending on the cryoprotectant. For instance, only one transition is observed for the maltodextrin solution (Figure 1(a)), while two transitions appear for the mixtures of polydextrose and glucose (Figures 1(b)–1(c)). These results are consistent with numerous previous studies, where solutions of LMW carbohydrates, such as glucose, fructose, sucrose, and trehalose, were found to exhibit two glass transition-like thermal events, while HMW polysaccharides, such as maltodextrin and starch, exhibited

Table 1: Distance-based experimental design for mixture of four components and measured response variables.

Exp No.	Run orden	X_M	X_G	X_P	X_W	T_g'	T_m'	T_m
1	1	0	0	0.6	0.4	-34.6	-22.6	-7.3
2	26	0.6	0	0	0.4	-6.3	-6.3	0.5
3	3	0	0.6	0	0.4	-54.2	-39.2	-15.4
4	4	0.017	0.017	0.017	0.95	N.D.	N.D.	1.8
5	29	0.2	0.2	0.2	0.4	-48.5	-36.1	-15.2
6	12	0.325	0	0	0.675	-7.1	-7.1	1.0
7	8	0	0.325	0	0.675	-53.4	-30.1	-3.9
8	27	0	0	0.325	0.675	-32.7	-20.1	-0.3
9	7	0.4	0.2	0	0.4	-38.6	-18.4	-2.1
10	17	0.2	0.4	0	0.4	-49.7	-28.6	-6.2
11	16	0.4	0	0.2	0.4	-29.9	-14.9	-1.0
12	10	0.2	0	0.4	0.4	-30.1	-16.9	-1.4
13	30	0	0.4	0.2	0.4	-47.2	-28.4	-9.5
14	20	0	0.2	0.4	0.4	-44.8	-29.4	-11.3
15	28	0.108	0.108	0.108	0.675	-38.9	-24.3	-0.6
16	22	0.217	0.2	0	0.583	-40.2	-25.0	-2.5
17	14	0.217	0	0.2	0.583	-25.6	-11.5	1.5
18	24	0	0.217	0.2	0.583	-45.7	-28.1	-4.7
19	11	0.354	0.054	0.054	0.538	-23.8	-14.1	-0.4
20	25	0.054	0.354	0.054	0.538	-51.3	-36.1	-5.4
21	6	0.054	0.054	0.354	0.538	-39.2	-20.5	-2.8
22	19	0.079	0.054	0.054	0.813	-37.0	-21.1	1.1
23	21	0.154	0.154	0.154	0.538	-40.4	-27.0	-1.9
24	23	0.217	0.017	0	0.767	-23.1	-11.0	1.1
25	9	0.017	0.217	0.000	0.767	-51.7	-30.3	-1.3
26	15	0	0	0.6	0.4	-36.5	-22.5	-7.1
27	2	0	0.6	0	0.4	-54.3	-39.2	-15.6
28	5	0.6	0	0	0.4	-7.3	-7.3	1.8
29	18	0.2	0	0.4	0.4	-32.2	-14.4	-1.9
30	13	0	0.2	0.4	0.4	-45.8	-30.0	-11.9

N.D.: not detected.

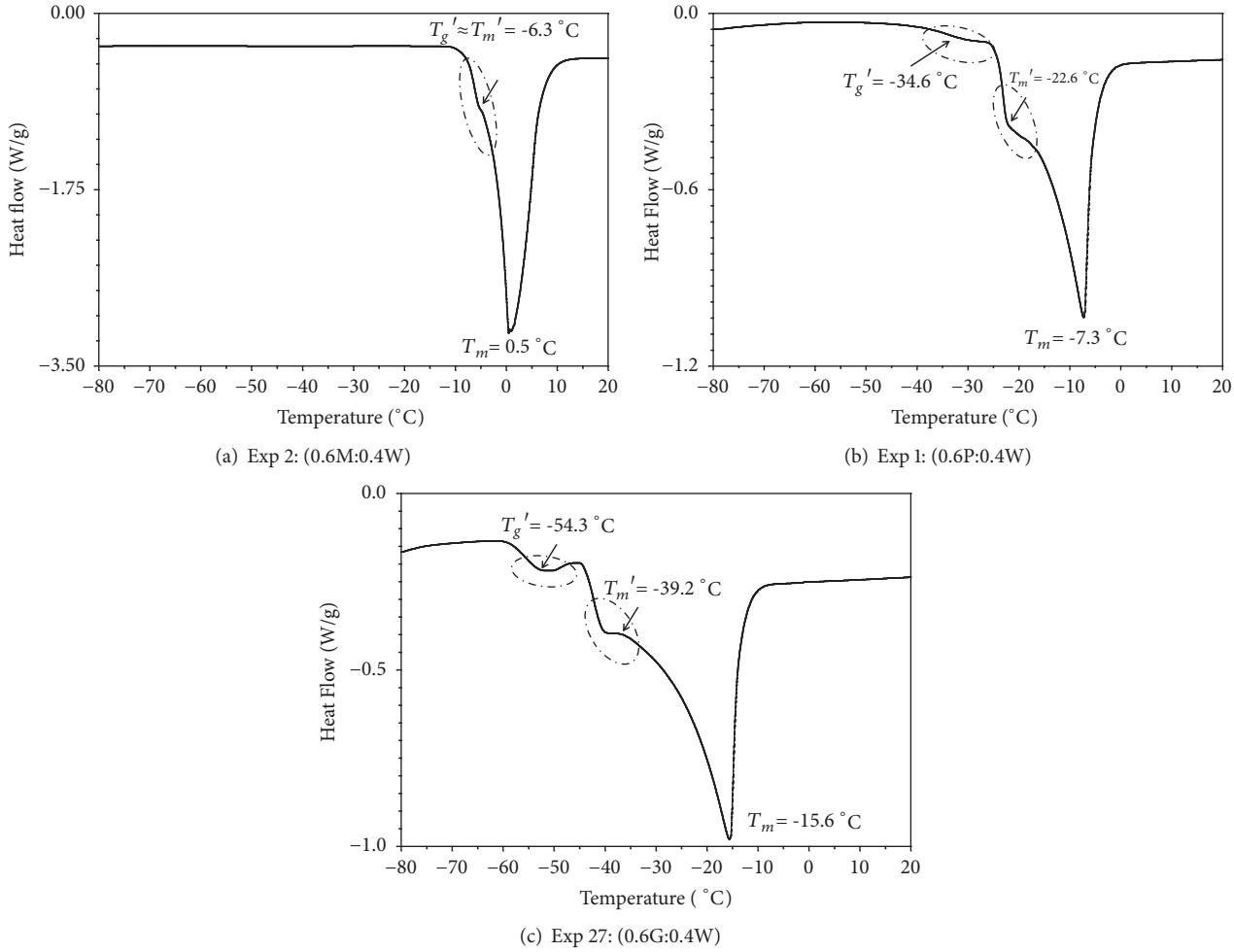

Figure 1: Phase and state transition analysis of frozen cryoprotectant solutions containing pure components prepared at a moisture content of 40% wet basis (X_W = 0.4) and annealed for 30 min at (T_m' − 1)°C: (a) Exp 2, (b) Exp 1, and (c) Exp 27.

a single transition by DSC analysis [20, 30, 32, 43, 51–55]. The origin of these two glass transitions is not completely understood; notions such as incompatibility of different solutes in the mixture, unequilibrated phases trapped around or within nucleated ice crystals, and reduced mobility of some components have been proposed to explain these transition events [51]. For aqueous sugar solutions, it has been suggested that the first transition can be attributed to a glass transition of the maximally freeze-concentrated phase, designated as T_g', while the second transition can be interpreted as the beginning of the melting of ice crystals, often designated as T_m' [30, 32, 33, 50–52]. In the case of protein aqueous solutions, it has been suggested that the first transition corresponds to a glass transition of part of unfrozen water, while the second transition corresponds to a glass transition of the primary chain of the hydrated protein [32]. Thus, a similar approach to those used for sugar solutions was implemented for the determination of the T_g' and T_m' of cryoprotectant solutions.

On the other hand, it has been reported that maltodextrin solutions exhibit a broad glass transition temperature range, attributed to its large molecular weight, and that the difference between T_g' and T_m' is likely to be very small or even null, or the glass transition may overlap with the ice melting [20, 30, 55]. For example, it has been reported by Roos and Karel [30] that the higher the molecular mass of maltodextrin, the lower the difference between the T_g' and T_m' values. However, it is probable that additional factors, such as high viscosity, ability to trap and bind water, maltodextrin-water interactions, or the amount of nonfreezable water, may be involved [56]. Thus, for practical considerations in this study, the T_g' and T_m' values were considered to be identical when solutions of maltodextrin at 40% water were used, as shown in Figure 1(a).

As shown in Figure 1, frozen solutions of pure maltodextrin (Experiment 2, Table 1) exhibited higher values of T_g', T_m', and T_m (_6,–6.3 and 0.5°C) than those obtained for frozen solutions of polydextrose (Experiment 1: –34.6, –22.6, and –7.3°C) and glucose (Experiment 27: –54.3, –39.2, and –15.6°C) at the same water content; this can be attributed to the higher molecular weight of maltodextrin. Roos and Karel [30] also reported that decreasing DE in maltodextrins

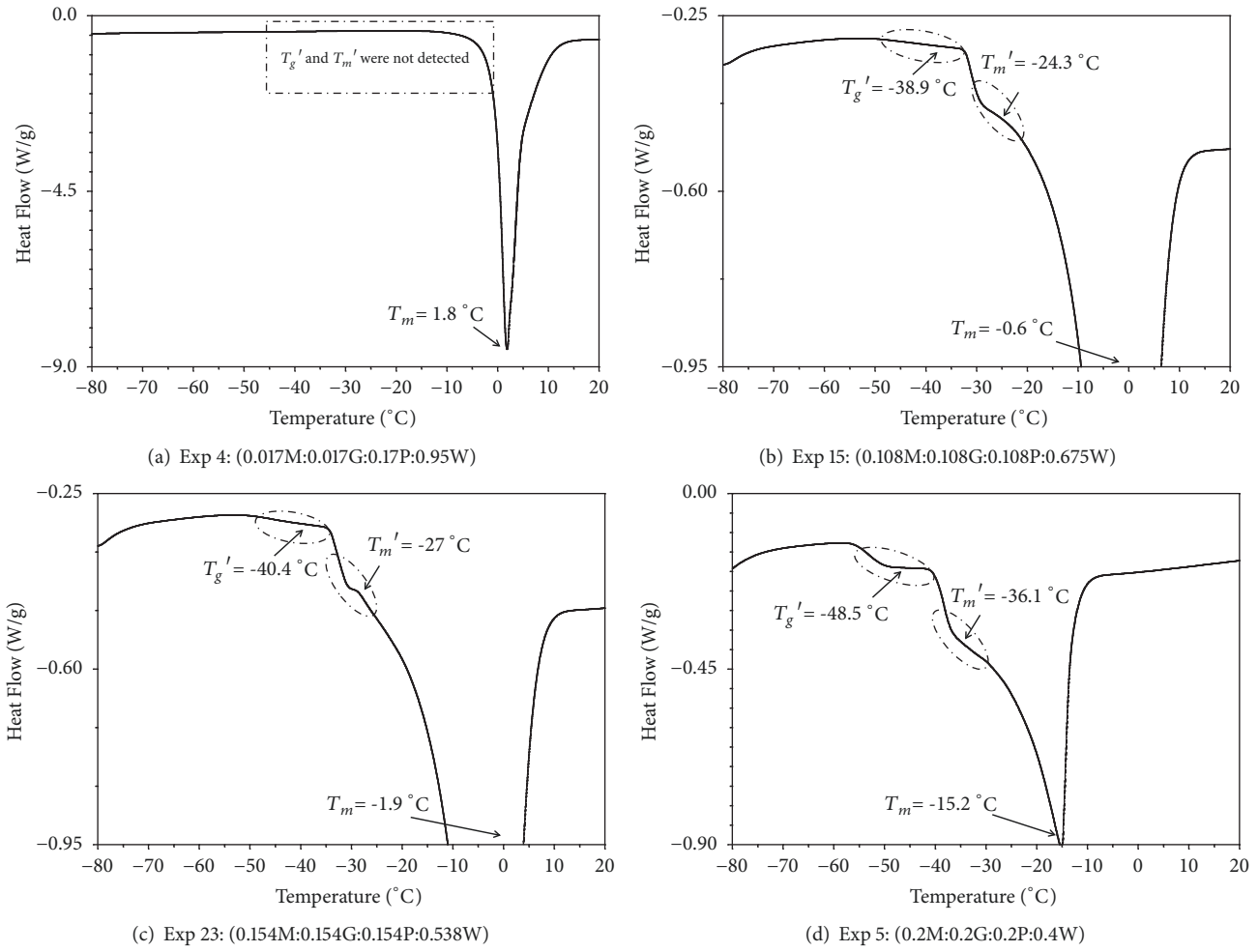

Figure 2: Phase and state transitions analysis of frozen ternary cryoprotectant solutions prepared at moisture contents in the range of 40–95% wet basis ($0.4 < X_W < 0.95$): (a) Exp 4, (b) Exp 15, (c) Exp 23, and (d) Exp 5. Exp 23 and Exp 5 were annealed for 30 min at (T_m' – 1)°C.

increased the molecular weight of the system and shifted the T_g' to a higher temperature. The T_g' and T_m' values determined for the pure maltodextrin solution prepared at 40% water are slightly higher than the values of T_g' (–15°C) and T_m' (–11°C) reported by Roos and Karel [30] when a solution of maltodextrin at 60% water with a similar DE of 5 was prepared. It is likely that the difference in the moisture content in the matrices is the main factor causing these discrepancies [12].

Typically, reports have shown that the higher the molecular weight of the cryoprotectant, the higher the T_g', T_m', and T_m values. The same trend has been reported in other studies when solutions of LMW and HMW carbohydrates were used [36, 43, 55]. In general, T_m' can be increased by addition of high molecular weight compounds as a result of an increase in the viscosity of the unfrozen phase which may delay crystallization of water [30, 57]. With regard to the T_m values, based on the colligative properties of a solution, the freezing point is directly proportional to the molal concentration of the solute [37]. This indicates that the lower the molecular mass of the solute, the higher the freezing point depression, as shown in Figure 1. Information on the freezing point depression is important for chilling and freezing processes, where reduction or inhibition of ice formation is required [3, 4].

For comparison, Figures 2(a)–2(d) show the DSC thermograms obtained for frozen ternary mixtures of cryoprotectants prepared with moisture contents in the range of 40–95% wet basis ($0.4 < X_W < 0.95$). The mixture containing 95% water (Figure 2(a), Experiment 4) showed no apparent glass transition events, because only the ice-melting peak was detected during heating. It is likely that the change in heat capacity (ΔC_p) at the glass transition range decreased with the solid content, resulting in T_g' and T_m' values for this sample outside the limits of detection [32, 54]. However, it was noted that the increase in the concentration of cryoprotectant solutions enhanced the intensity of thermal transitions, whereby the T_g' and T_m' values could be adequately determined in Experiments 15, 23, and 5 (Figures 2(b)–2(d)). It can also be observed in Figures 2(b)–2(d) that, at all moisture contents, the ternary mixtures exhibit well-defined global transitions, indicating good compatibility of the cryoprotectants [33, 56].

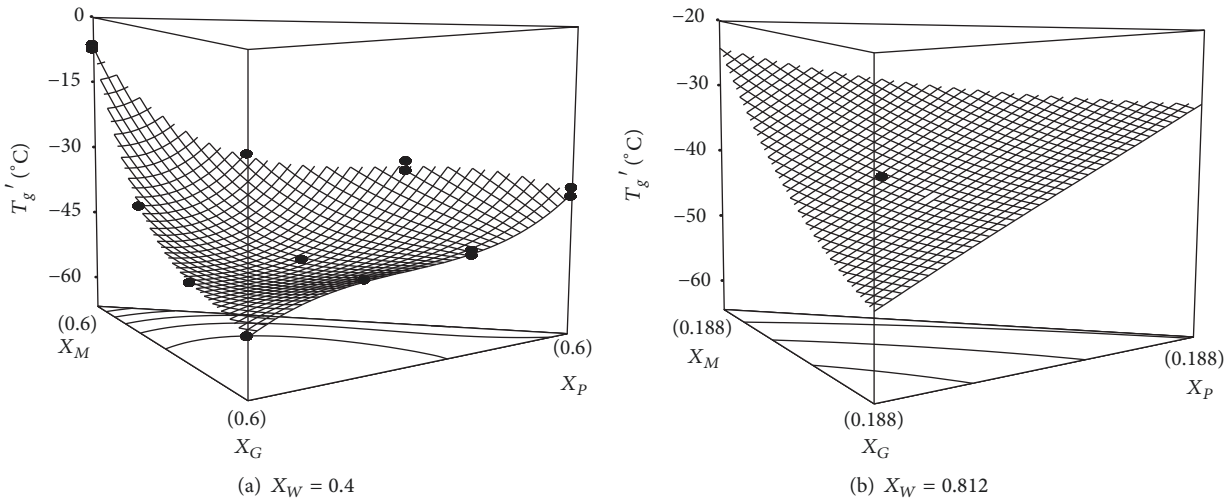

FIGURE 3: Response surface plots showing the variation of the experimental and predicted values of T_g' for different cryoprotectant solutions: (a) $X_W = 0.4$ and (b) $X_W = 0.812$. ● Experimental data.

The same behavior was observed for binary-component cryoprotectant solutions (DSC thermograms not shown).

The values of T_g', T_m', and T_m corresponding to each treatment are presented in Table 1. This table shows that the glass transition temperatures (T_g' and T_m') and freezing point (T_m) values vary from –54.3 to –6.3°C, –39.2 to –6.3°C, and –15.6 to 1.8°C, respectively. In general, these values are of the same order of magnitude as those reported in studies using similar saccharide solutions [30, 43, 55, 58]. According to the data in Table 1, no synergistic increase of T_g' and T_m' was found when mixtures of HMW and LMW cryoprotectants were analyzed. From Table 1, it can be observed that the highest T_g', T_m', and T_m values were found for solutions of maltodextrin at 40% water (Experiments 2 and 28) and the lowest values with solutions of glucose at 40% water (Experiments 3 and 27), with intermediate values for all the other cryoprotectant solutions. Typically, a mixture of compatible biopolymers exhibits intermediate state and phase transition temperatures because the components in the sample act as mutual plasticizers [56, 57]. Harnkarnsujarit et al. [47] had also reported that sugars such as sucrose, glucose and fructose depressed the T_m' and T_g' values of the maltodextrin-sugars systems.

3.2. Regression Analysis and Response Surface Plots. The uncoded regression coefficients, results of variance analysis (ANOVA), coefficients of determination (R^2), coefficients of variation (CV%), and model significance ($p > F$) obtained with (1) for T_g', T_m', and T_m are presented in Table 2. From these results, it can be observed that the response variables show a high level of significance for the regression equation ($p < 0.0001$), being nonsignificant for the lack of fit ($p > 0.05$), indicating the effectiveness of the regression analysis. Additionally, the R^2 values indicated that over 98% of the variability in the responses could be explained by the proposed models, also presented in Table 2.

According to the analysis of variance (Table 2), T_g', T_m', and T_m are all primarily affected by the linear terms of the cubic model, followed by interactions between binary and ternary components. Based on the literature, it is generally accepted that the T_m' and T_g' values are independent of the initial solute concentration or moisture content. The results from some studies have indicated that T_g' and T_m' exhibit slight variations according to the moisture content and, therefore, average values have been reported for several food products [20, 26, 30, 33]. However, the results from the present study show that the moisture content of the cryoprotectant solutions ($p < 0.0001$, Table 2) is also a crucial factor influencing these thermal parameters.

Three-dimensional response surface plots for T_g' (Figure 3), T_m' (Figure 4), and T_m (Figure 5) using two different moisture contents for each response variable were constructed in order to gain better understanding of the interactive effects of the three cryoprotectants (X_M, X_G, X_P) on the corresponding variables. The results presented in Figures 3–5 demonstrate that, in all cases, good agreement exists between the experimental and predicted values ($R^2 > 0.98$). Also, the profiles in Figures 3–5 show that, at all moisture contents, the maximum glass transition and freezing temperatures appear at the points corresponding to pure maltodextrin, while the minimum values were obtained for the samples containing pure glucose. The values in good agreement with the experimental results are presented in Table 1. From the point of view of the glass transition concept, this behavior suggests that maltodextrin exhibits a greater cryostabilizing effect than polydextrose and glucose. For instance, maltodextrin DE 18 showed a higher effectiveness against lipid oxidation that an equiproportional mixture of sucrose and sorbitol in frozen-stored minced muscle of Atlantic mackerel [44]. On the other hand, Rodríguez-Furlán et al. [43] found that inulin exhibits better stabilizing properties than glucose and sucrose in the preservation of

Table 2: Uncoded regression coefficients and variance analysis of the hierarchical mathematical models to evaluate the variation of response variables as a function of chemical composition of the cryoprotectant solutions ($p<0.05$).

Effect	Response variables					
	T_g'		T_m'		T_m^*	
	a values	p>t	*a* values	p>t	*a* values	p>t
X_M	-150.42	< 0.0001	-25.84	< 0.0001	542.57	< 0.0001
X_G	-51.85	< 0.0001	-42.15	< 0.0001	-425.77	0.2184
X_P	109.26	< 0.0001	-154.73	< 0.0001	-364.76	< 0.0001
X_W	-50.10	< 0.0001	-19.77	< 0.0001	490.96	< 0.0001
$X_M X_G$	127.35	< 0.0001	261.83	0.6304	233.10	0.3608
$X_G X_P$	-61.02	0.1873	111.71	0.1788	-45.29	0.8449
$X_P X_W$	-272.34	0.0190	279.03	0.9517	777.85	0.0197
$X_M X_W$	397.90	0.0008	69.14	0.0343	-314.98	0.2683
$X_G X_W$	-13.08	0.7631	-24.86	0.3756	335.40	0.2069
$X_M X_P$	-35.29	< 0.0001	-51.63	0.5986	-3827.75	0.0559
$X_M X_G X_P$	-427.34	0.0296	-1642.90	< 0.0001	-22925.84	< 0.0001
$X_M X_G X_W$	-580.60	0.0160	-672.41	0.0057	-	
$X_M X_P X_W$	-369.15	0.0817	345.36	0.1057	10794.51	0.0052
$X_G X_P X_W$	-281.90	0.3225	-	-	-	
$X_M X_G (X_M - X_G)$	-156.36	0.0171	-	-	-	
$X_M X_P (X_M - X_P)$	-271.59	0.0002	-137.14	0.0201	-2310.27	0.0241
$X_M X_W (X_M - X_W)$	166.11	0.1724	-	-		
$X_G X_P (X_G - X_P)$	130.49	0.0225	183.97	0.0037	2801.85	0.0079
$X_G X_W (X_G - X_W)$	-	-	-	-	-	-
$X_P X_W (X_P - X_W)$	-328.21	0.0311	234.05	0.0942	-	-
Models						
p>F		< 0.0001		< 0.0001		< 0.0001
R^2		0.9971		0.9907		0.9849
Lack of fit		0.2205		0.1066		0.2302
C.V. (%)		3.38		5.90		8.57

∗Note: according to a Box-Cox analysis, a transformation $Tm* = (Tm + 20)^2$ on Tm values was carried out to stabilize the variance.

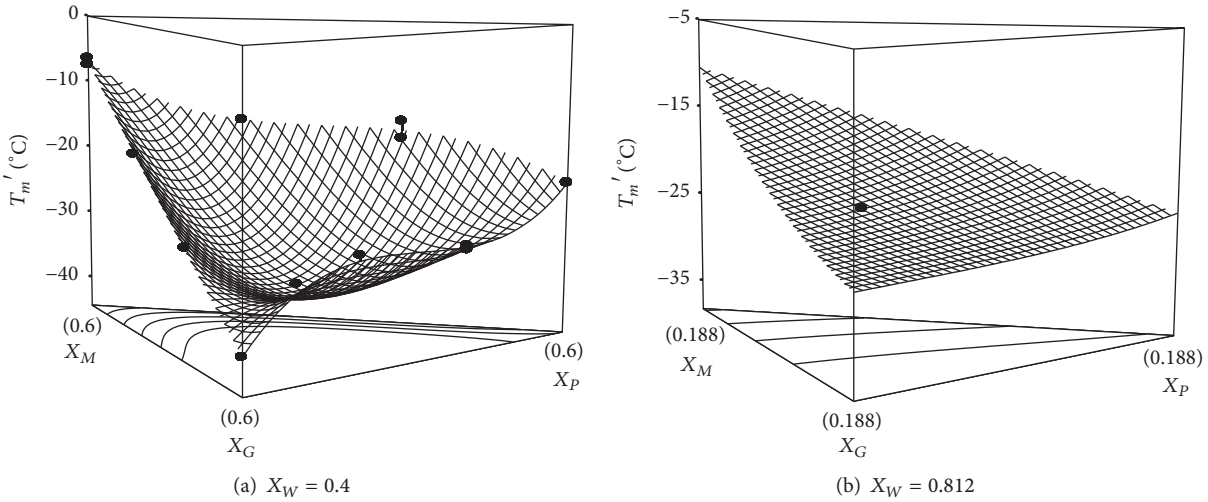

FIGURE 4: Response surface plots showing the variation of the experimental and predicted values of T_m' for different cryoprotectant solutions: (a) X_W = 0.4 and (b) X_W = 0.812. ● Experimental data.

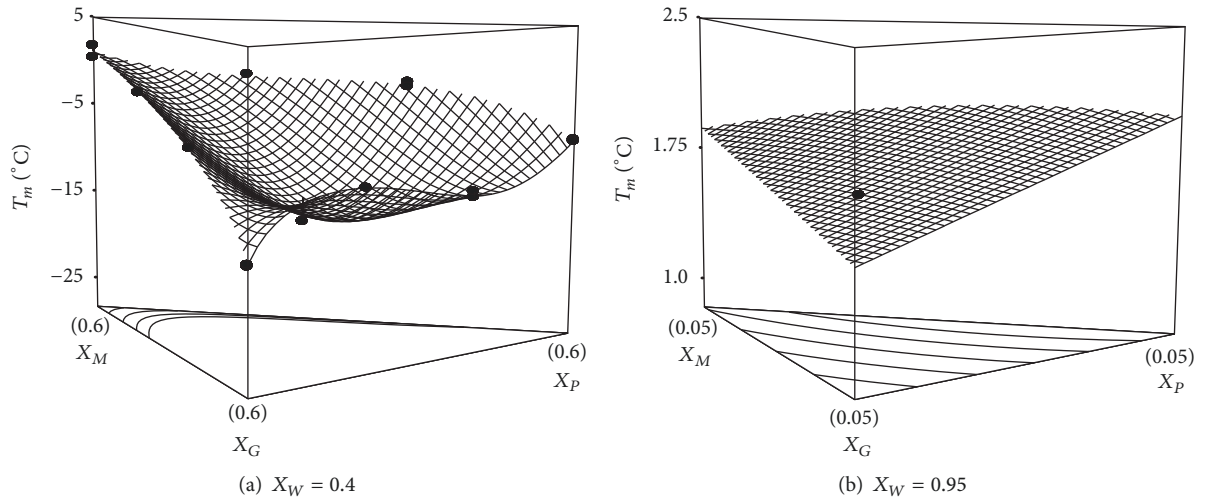

FIGURE 5: Response surface plots showing the variation of the experimental and predicted values of T_m for different cryoprotectant solutions: (a) X_W = 0.4 and (b) X_W = 0.95. ● Experimental data.

frozen bovine plasma protein. However, it is also clearly shown that glucose significantly contributes to the depression of the freezing point in aqueous cryoprotectant solutions and that it can be used as an alternative to reduce or avoid intra- or extra-cellular ice formation during chilling and freezing processes [3, 4]. As previously discussed, intermediate values of T_g, T_m', and T_m were obtained for the other mixtures of cryoprotectants, resulting from the good compatibility and mutual plasticizing action of the different components in the samples [56, 57].

Although numerous studies have been conducted on the use of cryoprotectants to prevent deleterious changes in foods caused during freezing and frozen storage, little research has been carried out on the thermal transition properties of aqueous cryoprotectant solutions at frozen temperatures at a large working range of water contents. In this context, the experimental values of T_g', T_m', and T_m (Table 1) obtained and the mathematical models proposed in this study (Table 2) may be a great aid for the formulation of cryoprotective media containing more than two cryoprotectants to improve the storage stability and quality of frozen food products with high and intermediate moisture content and modifiable formulations, such as ice cream, purees, jams, surimi, sugared yolks, etc. However, further studies are required, which will focus on overcoming the difficulties in the incorporation of cryoprotectants in large samples or foodstuffs, such as whole fruits and meats.

4. Conclusions

The effects of cryoprotectants and their concentration on the glass and phase transition temperatures of frozen aqueous solutions containing maltodextrin, polydextrose, glucose, and their mixtures prepared at moisture contents in the range

of 40–95% water were studied. DSC thermograms revealed the existence of a glass transition for pure maltodextrin solutions and two transitions for all the other solutions. The results indicated that the T_g', T_m', and T_m values increase with the molecular weight of the cryoprotectant. Additionally, statistical analysis of the data ($p < 0.05$) demonstrated that both the solute and water composition should be considered in the formulation of cryoprotective media, as they were found to significantly affect the T_g', T_m', and T_m values ($p < 0.05$). Mathematical expressions for T_g', T_m', and T_m as a function of the mass fractions of the cryoprotectants (X_M, X_G, X_P) and water (X_W) and their interactions were developed to guide the formulation of cryoprotective media involving mixtures of more than two cryoprotectants to improve the storage stability and quality of frozen food products at high and intermediate moisture contents with modifiable formulations, such as ice cream, purees, jams, surimi, sugared yolks, etc.

Data Availability

Data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare no conflicts of interest.

Acknowledgments

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RESUMEN EN EXTENSO 2

The Influence of Maltodextrin on the Thermal Transitions and State Diagrams of Fruit Juice Model Systems

INTRODUCCIÓN

Un diagrama de estado es una representación gráfica de los distintos estados físicos y transiciones de fase/estado que ocurren en un material en función del contenido de sólidos y la temperatura (Rahman, 2010). El diagrama de estado generalmente, incluye la curva de congelación en función del contenido de solidos (T_m vs X_s), la curva de transición vítrea en función del contenido de solidos (T_g vs X_s) y la condición de máxima crio-concentración. Estos diagramas han sido de gran ayuda para monitorear el progreso y desarrollo de varias operaciones unitarias como la congelación, el almacenamiento en congelado, liofilización, crio-concentración, deshidratación y secado por aspersión, que se utilizan para extender la vida útil de los alimentos y generar una gama de productos de frutas de humedad alta, intermedia y baja. En este contexto, la curva del punto de congelación (T_m vs X_s) y las temperaturas de transición de fase máximamente crioconcentrada T_g' y T_m' pueden ser utilizadas para prevenir cambios físicos, químicos y estructurales que tienen lugar durante el almacenamiento en congelado de frutas frescas, y para evitar la reducción de volumen o colapso del alimento que se presenta durante la liofilización de materiales biológicos (Celli et al., 2016). Las temperaturas T_g' y T_m' son consideradas como parámetros de referencia para determinar la estabilidad de los alimentos congelados, porque se produce la máxima formación de hielo cuando los sistemas alimentarios se almacenan a estas temperaturas. Por otro lado, la relación T_g y X_s se ha considerado en la literatura como parámetro de referencia para determinar las condiciones adecuadas de proceso de secado y la estabilidad de almacenamiento de productos de baja humedad (Bhandari & Howes. 1999). En estos casos, las transformaciones estructurales dependientes tiempo, como la adherencia y deposición que ocurren en el sacado por aspersión o el apelmazamiento y los

fenómenos de cristalización que tienen lugar durante el almacenamiento de frutas en polvo, depende en gran medida del valor T_g. En la literatura se ha encontrado que los valores T_g', T_m' y T_g de los productos de fruta son muy bajo del orden de -71 a -38°C, -52 a -26°C, y de 12 a 75°C, respectivamente. Se ha recomendado el uso de polímeros como crioprotectores durante el almacenamiento en congelado y como agente acarreador en los procesos de secado para manipular el estado físico y elevar deliberadamente los valores de T_g', T_m' y la T_g de los alimentos (Flores-Ramírez et al., 2019). El uso de carbohidratos de alto peso molecular en la construcción de diagramas de estado para productos de frutas no se ha explorado ampliamente. Solo han sido algunos estudios que han informado de diagramas de algunas frutas con maltodextrina. Ya que los componentes solidos de las frutas son glucosa, fructosa, sacarosa, ácido cítrico y pectina se planteó hacer sistemas modelos basados en las diversas composiciones de las diferentes variedades de frutas (Fabra et al., 2009). Esto con la finalidad de controlar la composición de cada sistema y evaluar el efecto de la maltodextrina sobre los valores de T_g', T_m' y la T_g.

OBJETIVOS

1. Evaluar el efecto de la maltodextrina en los valores de T_g ', T_m', T_m y T_g de diferentes sistemas de modelos de jugos de frutas preparados con diversos contenidos de agua mediante el uso de calorimetría diferencial de barrido (DSC),
2. Construir los diagramas de estados de diferentes sistemas modelo de jugos de frutas.
3. Evaluar la influencia de la composición química en las transiciones térmicas T_g', T_m', T_m y T_g.

MATERIALES Y MÉTODOS

Glucosa, fructosa, sacarosa, pectina y ácido cítrico fueron utilizados para formular sistemas modelo de jugos de frutas adicionados con fracciones másicas de maltodextrina de 0 a 0.8. Un diseño D-Optimal para mezclas de 6 componentes fue

utilizado con las siguientes restricciones: $0 \leq X_M \geq 0.8$; $0 \leq X_P \geq 0.15$; $0 \leq X_A \geq 0.15$; $X_G+X_S+X_F+X_A+X_P+X_M=1$.Un total de 25 sistemas anhidros fueron obtenidos. Para la obtención de los diferentes diagramas de estado fue necesario un acondicionamiento de los sistemas modelo anhidros. Para humedades menores a 50% se realizó mediante exposición directa a humedad relativa del 100 %. Para muestras con humedades superiores a 50% se realizó el acondicionamiento mediante la adición directa de agua. Muestras de 10 mg fueron tomadas de cada sistema modelo acondicionado y colocadas en charolas DSC (TA Instruments), las cuales fueron selladas herméticamente y se dejaron en equilibrio durante 24 horas. Todos los análisis térmicos fueron realizados en un Calorímetro Diferencial de Barrido (DSC Q2000 (TA Instruments). Las muestras fueron sometidas a un método de escaneo convencional lineal el cual consistió en un enfriamiento a -90°C a una velocidad de 20°C/min, esta temperatura se mantuvo durante 5 min, y posteriormente fueron calentadas hasta 20°C a 10°C/min. Para muestras con una humedad de 20-50 % (b.h.) fue requerido un procedimiento de annealing a Tm'-1°C con el fin de maximizar la formación de hielo. Mientras que para muestras con XM predominante, fue necesario someter las muestras a un calentamiento desde la temperatura ambiente hasta 80°C a 20°C/min. Para muestras anhidras o muestras con agua no congelable el protocolo de melt-quenching fue utilizado. Los valores de T_g' y T_m' fueron respectivamente asignados al punto medio del 1° y 2° paso de cambio de flujo de calor observados en los termogramas durante el calentamiento. La temperatura máxima correspondiente a la endoterma de fusión fue considerada como el punto de congelación (T_m). Posteriormente se realizaron los diagramas de estado para cada sistema modelo y se obtuvieron los modelos de las curvas T_m y T_g con la ecuaciones de Chen y Gordon- Taylor, respectivamente.

RESULTADOS

En los diferentes sistemas modelo de jugos de frutas preparados en rangos de agua congelable entre 30 al 90% en base húmeda, mostraron tres eventos térmicos en los que el pico endotérmico de fusión del hielo fue el rango más visible, así mismo

se visualizaron dos cambios en la línea base característicos de transición de estado. Para soluciones de azúcar se ha sugerido que la primera transición de estado se atribuye a la transición vítrea de la fase máximamente crioconcentrada (T_g') y la segunda transición considerarse como el comienzo del derretimiento de los cristales de hielo (T_m'). La primera transición se observó en los diferentes sistemas modelos en rangos de -9.5 a -57.1°C, y la segunda transición entre -9.5 a -42.8°C. Los valores más altos fueron obtenidos en sistemas modelo con fracciones másicas de maltodextrina superiores o iguales a 0.4. Con lo que respecta a los sistemas modelo acondicionados a humedades reducidas de 0 a 29% base húmeda, se pudo observar que las muestras presentaron un desplazamiento endotérmico debido a la transición vítrea con valores de 157 a -0.3°C. Cuanto mayor fue la concentración de sólidos, los valores de T_g de los sistemas modelo fueron más elevados. La transición vítrea se produjo en un amplio rango de temperatura (alrededor de 40-50°C), esto debido a la presencia de maltodextrina. Los diagramas de estado obtenidos fueron afectados significativamente ($p<0.05$) por la composición química de los sistemas modelo, además se observó un aumento en el valor de los parámetros t_g', t_m' y t_g con lo cual los valores de estos parámetros están más cercanos a los rangos de temperatura utilizados en los procesos de congelación y deshidratación. Así mismo, se obtuvieron modelos matemáticos que permiten estimar el valor de los parámetros de los diagramas de estado en función de la composición de solidos de las frutas, por lo que es posible construir diagramas de estado y predecir los efectos q tendrá la adición de maltodextrina sobre una amplia gama de productos derivados de las frutas.

CONCLUSIÓN

Se investigaron los efectos de la adición de maltodextrina sobre T_g', T_m', T_m y T_g durante la construcción de diagramas de estado de varios sistemas de modelos de jugo de frutas. El aumento de la fracción másica de maltodextrina dio como resultado un aumento significativo de las transiciones térmicas antes mencionadas. Sin embargo, se requieren fracciones de masa superiores a 0,4 para inducir un aumento

significativo de T_g', T_m', T_m y la curva T_g. La maltodextrina, por tanto, puede considerarse como una buena alternativa en la formulación de medios crioprotectores para una adecuada conservación congelada de alimentos de humedad alta e intermedia, y como agente portador en el proceso de secado por atomización. Los modelos matemáticos desarrollados facilitaron la determinación de la influencia de la composición química sobre los valores T_{gs} , K, E, B, T_m, T_g', T_m' y x_s', y también podría utilizarse para predecir los diagramas de estado de muestras en función de la concentración de solutos predominantes en jugos de frutas y la fracción másica de maltodextrina, ayudando en el diseño y optimización de procesos y procedimientos de almacenamiento de productos frutales en rangos de humedad alta, intermedia y baja.

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RESUMEN GRÁFICO 2

Sistemas modelo de jugos de frutas

Acondicionamiento de humedad

Humedad baja 1–29 %
Humedad intermedia 30– 50%

Humedad alta 60 – 90 %

Análisis calorimétrico

Caracterización térmica de sistemas modelo

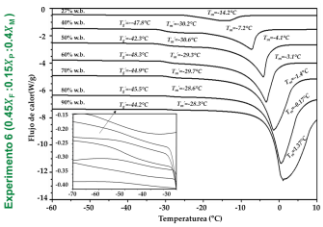
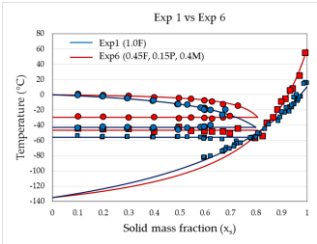


Diagrama de estado



polymers

MDPI

Article

The Influence of Maltodextrin on the Thermal Transitions and State Diagrams of Fruit Juice Model Systems

Pedro García-Coronado [1], Alma Flores-Ramírez [1], Alicia Grajales-Lagunes [1], Cesar Godínez-Hernández [2], Miguel Abud-Archila [3], Raúl González-García [1] and Miguel A. Ruiz-Cabrera [1,*]

1 Faculty of Chemical Sciences, Autonomous University of San Luis Potosí, Manuel Nava 6, 78290 San Luis Potosí, Mexico; pgarciam16@gmail.com (P.G.-C.); aalmaramirez@hotmail.com (A.F.-R.); grajales@uaslp.mx (A.G.-L); raulgg@uaslp.mx (R.G.-G.)

2 Desert Zones Research Institute, Autonomous University of San Luis Potosí, Altair 200, 78377 San Luis Potosí, Mexico; cesar.godinez@uaslp.mx

3 National Institute of Technology of Mexico, Technological Institute of Tuxtla Gutiérrez, Street Km 1080, Tuxtla Gutiérrez 29050, Mexico; miaba69@hotmail.com

* Correspondence: mruiz@uaslp.mx

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Abstract: The state diagram, which is defined as a stability map of different states and phases of a food as a function of the solid content and temperature, is regarded as fundamental approach in the design and optimization of processes or storage procedures of food in the low-, intermediate-, and high-moisture domains. Therefore, in this study, the effects of maltodextrin addition on the freezing points (T'_m, T_m) and glass transition temperatures (T'_g, T_g) required for the construction of state diagrams of fruit juice model systems by using differential scanning calorimetry methods was investigated. A D-optimal experimental design was used to prepare a total of 25 anhydrous model food systems at various dry mass fractions of fructose, glucose, sucrose, pectin, citric acid, and maltodextrin, in which this last component varied between 0 and 0.8. It was found that maltodextrin mass fractions higher than 0.4 are required to induce significant increases of T'_g, T'_m, T_g, and T_m curves. From this perspective, maltodextrin is a good alternative as a cryoprotectant and as a carrier agent in the food industry. Furthermore, solute-composition-based mathematical models were developed to evaluate the influence of the chemical composition on the thermal transitions and to predict the state diagrams of fruit juices at different maltodextrin mass fractions.

Keywords: state diagrams; maltodextrin; thermal transitions; DSC; model systems

1. Introduction

A state diagram is a graphical map of the different states of a food or biomaterial as a function of temperature over the entire solid mass fraction scale of materials containing freezable and unfreezable water [1–4]. In this context, a state diagram usually includes the freezing curve as a function of the solid content (T_m vs. w_s), the glass transition curve as a function of the solid content (T_g vs. w_s), and the maximal-freeze-concentration condition, defined by the onset melting temperature of ice crystals (T'_m), the glass transition temperature at maximum ice formation conditions (T'_g), and the solid mass fraction (w'_s) [1–4]. These diagrams have been of great help in monitoring the progress and development of various employed unit operations, such as freezing, frozen storage, lyophilization, cryoconcentration, dehydration, and spray drying, which are all used to extend shelf life and to generate a range of high-, intermediate-, and low-moisture fruit products, such as whole fruits, cut fruits, juices, purees, jams,

marmalades, dried fruits, powders, and leathers [1,2,4–9]. For instance, the freezing curves (T_m vs. w_s) and the freeze-concentrated unfrozen phase transition temperatures T'_g and T'_m of products can be used to prevent physical, chemical, and structural changes that take place during the frozen storage of fresh and cut fruits and to avoid the product shrinkage or collapse usually observed during the freeze drying of biological materials [5,10–14]. The temperatures T'_g and T'_m are regarded as reference parameters determining the stability of frozen foods, because maximum ice formation takes place when food systems are stored between these temperatures [2,15]. As a general statement, the formation of a glassy vitreous state is then required in frozen storage to prevent molecular motion and further crystallization of water into ice, as well as in freeze drying, because collapse during primary drying will occur when the product temperature exceeds the collapse temperature, which is normally a few degrees above the T'_g value [10–14]. On the other hand, the relationship between T_g and w_s in the solid mass fraction domain of $w'_s \leq T_g \leq 1$ has also been regarded in the literature as a reference parameter determining the suitable conditions of drying processes and the storage stability of low-moisture food products. In these cases, the various time-dependent structural transformations, such as the stickiness and deposition events occurring on the dryer surface during spray drying or caking and the crystallization phenomena that take place during fruit powder storage, are highly dependent on T_g values [16,17].

For these purposes, several state diagrams of pure components, model food systems, and real fruit products have been reported in the literature [4,18–26]. Nevertheless, from the above studies it was found that fruit products presented very low T'_g, T'_m, and anhydrous sample glass transition $\left(T_{gs}\right)$ values, which ranged from −71 to −38 °C, from −52 to −26 °C, and from 12 to 75 °C, respectively. Thus, it is sometimes not possible to design suitable, efficient, and economical processes and frozen storage procedures for sugar-rich products such as fruits [2,11]. The use of polymers as cryoprotectants during frozen storage and as carrier agents in spray drying processes to manipulate the physical state and deliberately elevate the T'_g, T'_m, and T_g of foods has been widely recommended [11,27–32]. Typically, polymers with high molecular weight (HMW), such as maltodextrin, polydextrose, hydrocolloids, and gum, have been used [11,14,28–33]. The use of HMW carbohydrates in the construction of state diagrams for fruit products has not been explored extensively, and there are only a few studies in which the state diagrams of some fruits with a maltodextrin addition have been reported [34–36]. On the other hand, water and soluble solids such as sugars, pectin, and organic acids are the main fruit components, and the amount of each of these constituents can change drastically from one fruit to another. Furthermore, the number of possible fruit compositions is great. Therefore, experiments with fruit juice model systems with controlled chemical compositions are required. The aim of the present work is (i) to evaluate the effect of maltodextrin on the T'_g, T'_m, T_m, and T_g values of different fruit juice model systems prepared with various water contents by using differential scanning calorimetry (DSC), (ii) to construct the corresponding state diagrams, and (iii) to evaluate the influence of the chemical composition on the abovementioned thermal transitions.

2. Materials and Methods

2.1. Materials

Analytical-grade maltodextrin dextrose equivalent 4–7 (product No. 419672; molecular weight (MW) 3600, Sigma-Aldrich Co. St. Louis, MO, USA), crystalline fructose (product No. F2543; MW 180.16, Sigma-Aldrich Co. St. Louis, MO, USA), glucose (product No. G7528; MW 180.2, Sigma-Aldrich Co. St. Louis, MO, USA), sucrose (product No. S0389; MW 342.3, Sigma-Aldrich Co. St. Louis, MO, USA), citric acid (product No. 251275; MW 192.12, Sigma-Aldrich Co. St. Louis, MO, USA), and pectin from apples (product No. 76282, MW 208.2, Sigma-Aldrich Co. St. Louis, MO, USA) were purchased and used without further treatment in the experiments.

2.2. Preparation of Fruit Juice Model Systems

A completely randomized D-optimal experimental design for mixtures of six components was used to prepare a total of 25 anhydrous model food systems at various dry mass fractions of fructose (X_F), glucose (X_G), sucrose (X_S), citric acid (X_A), pectin (X_P), and maltodextrin (X_M), as shown in Table 1. The studies carried out by Grajales-Lagunes et al. [4] and Fongin et al. [37,38] were considered as references to establish the mass fractions of citric acid ($0 \leq X_A \leq 0.15$), pectin ($0 \leq X_P \leq 0.15$), and maltodextrin ($0 \leq X_M \leq 0.8$) in the model food systems.

Table 1. D-optimal experimental design for a mixture of six components and the elaboration of anhydrous model food systems.

Experiment		Mass Fractions					
no.	Ro	X_F	X_G	X_S	X_P	X_A	X_M
1	15	1	0	0	0	0	0
2	6	0	1	0	0	0	0
3	8	0	0	1	0	0	0
4	4	0	0	0	0.15	0.05	0.80
5	1	0.283	0.283	0.283	0.075	0.075	0
6	7	0.45	0	0	0.15	0	0.40
7	21	0	0.45	0	0.15	0	0.40
8	2	0	0	0.45	0.15	0	0.40
9	23	0.50	0	0.50	0	0	0
10	22	0	0.50	0.50	0	0	0
11	18	0.50	0.50	0	0	0	0
12	24	0.145	0.145	0.145	0.059	0.15	0.355
13	20	0.70	0	0	0.15	0.15	0
14	5	0	0.70	0	0.15	0.15	0
15	11	0	0	0.70	0.15	0.15	0
16	25	0.327	0.327	0.077	0.035	0.035	0.198
17	19	0.327	0.077	0.327	0.035	0.035	0.198
18	12	0.077	0.327	0.327	0.035	0.035	0.198
19	3	0.177	0.077	0.077	0.035	0.035	0.598
20	9	0.502	0.077	0.077	0.035	0.110	0.198
21	13	0.077	0.540	0.077	0.035	0.073	0.198
22	14	0.077	0.077	0.577	0.035	0.035	0.198
23	10	0.35	0.35	0	0.15	0.15	0
24	17	0.35	0	0.35	0.15	0.15	0
25	16	0	0.35	0.35	0.15	0.15	0

no = number, Ro = Run order.

In order to obtain uniform mixing for the component mixtures, the procedure of complete dissolution followed by freeze drying was used for each of the model systems. Thus, solutions with 60% water were prepared, then frozen at −60 °C using a laboratory freezer (ScientTemp Model 86-01A Adrian, Michigan, USA) for 24 h and dried at −40 °C with a 5-mTorr vacuum using a freeze dryer (IlshinBioBase, TFD8501, Seoul, Korea). After complete drying, the freeze-dried mixtures were transferred to a pestle and mortar where they were ground into a fine powder. These samples were then equilibrated over Drierite® (anhydrous calcium sulfate, aw ≈ 0) in desiccators at room temperature for at least 4 weeks to obtain completely dried samples. Afterwards, these equilibrated freeze-dried mixtures were conditioned in the low, intermediate, and high moisture domains following the methodologies proposed by Grajales-Lagunes et al. [4] and Ruiz-Cabrera et al. [22], then subjected to the calorimetric analysis described below, in which the freezing points (T'_m, T_m) and glass transition temperatures (T'_g, T_g) for various water contents were determined.

2.3. Determination and Modeling of the Thermal Transition by DSC

A Q2000 differential scanning calorimeter (TA Instruments, New Castle, Delaware, USA) equipped with an RCS90 cooling system and Universal Analysis 2000® software for data treatment were used. The measurements were carried out in an inert atmosphere using nitrogen at a flow rate of 50 mL/min. An empty DSC pan as a reference and samples of about 10 mg were used in all of the cases. The standard mode with the linear temperature program was used to determine the freezing points and glass transition temperatures in samples containing freezable water [4,26]. Samples contained in sealed pans were cooled at 20 °C/min from room temperature to −90 °C, equilibrated for 5 min, and then heated to 20 °C at a heating rate of 10 °C/min. For the samples in the concentration range of 20% and 50% water, the previous calorimetry protocol was used with annealing at the apparent value of the freezing point (T'_m−1 °C) as the additional treatment to maximize ice formation in the samples [4,26]. In these cases, the samples were then equalized in the DSC at 20 °C, cooled to −90 °C at 20 °C/min, held for 2 min, warmed at 20 °C/min to the annealing temperature (T'_m−1 °C), kept for 30 min, recooled to −90 °C at 20 °C/min, held for 5 min, and finally scanned to 20 °C at 10 °C/min. The T'_g and T'_m values were assigned to the midpoint of the first and second step changes, respectively, of the observed heat flow and temperature relationship during the heating process, whereas the freezing point (T_m) was determined from the peak temperature in the melting endotherm [4,22,26]. For anhydrous solids and samples containing unfreezable water, the calorimeter melt-quenching protocol was used [4,22]. The samples contained in sealed pans were first equilibrated in the DSC at 20 °C, then heated at 20 °C/min to the corresponding melting temperature using a holding time of 2 min. Afterwards, the samples were cooled to −90 °C at 20 °C/min and maintained there for 2 min. Finally, the samples were reheated at 10 °C/min again to the corresponding melting temperature. The midpoint T_g value was determined using the half-height method from the reheating DSC thermograms.

In order to construct state diagrams for each model system, the Gordon–Taylor (G-T) equation (Equation (1)) and Chen equation (Equation (2)) were used to model the glass transition curve (T_g vs. w_s) and freezing point curve (T_m vs. w_s), respectively, as follows [2,21,26]:

$$T_{gm} = \frac{w_s T_{gs} + K(1 - w_s) T_{gw}}{w_s + K(1 - w_s)} \quad (1)$$

$$T_m = T_w + \left(\frac{\beta}{\lambda_w}\right) ln\left(\frac{1 - w_s - B w_s}{1 - w_s - B w_s + E w_s}\right) \quad (2)$$

In Equation (1), T_{gm}, T_{gs}, and T_{gw} are the glass transition temperatures of the sample, anhydrous solids, and amorphous water (−135 °C), respectively. In addition, w_s is the mass fraction of solids and K is a constant parameter denoting the strength of the interaction between the water and the food solids [1,2]. In Equation (2), T_m and T_w are the freezing temperatures of the sample and pure water, respectively; β is the molar freezing point constant of water (1860 kg K/kgmol) [2,21,26]. Moreover, λ_w and λ_s are the molecular mass values of water and solids, respectively; E is the molecular mass ratio of water-to-solids ($\frac{\lambda_w}{\lambda_s}$). Finally, B is the ratio of unfreezable water from the total solid content. A nonlinear regression analysis by the least squares method was performed to estimate the parameters T_{gs}, K, E, and B by using Microsoft Excel (2016). The goodness of the fitted models was determined by the coefficient of determination (R^2).

On the other hand, the procedure proposed by Grajales-Lagunes et al. [4] and Zhao et al. [26] was used to estimate the corresponding average values of T'_g and T'_m, as well as the values of w'_s from each of the constructed state diagrams.

2.4. Statistical Analysis

A polynomial equation (Equation (3)) was used to evaluate the effects of the weight fractions of fructose (X_F), glucose (X_G), sucrose (X_S), citric acid (X_A), pectin (X_P) and maltodextrin (X_M) on the parameters T_{gs}, K, E, B, T'_g, T'_m, and w'_s, as follows:

$$\begin{aligned} y = {} & a_1X_F + a_2X_G + a_3X_S + a_4X_p + a_5X_A + a_6X_M + a_7X_FX_G + a_8X_FX_S + a_9X_FX_P \\ & + a_{10}X_FX_A + a_{11}X_FX_M + a_{12}X_GX_S + a_{13}X_GX_P + a_{14}X_GX_A + a_{15}X_GX_M \\ & + a_{16}X_SX_P + a_{17}X_SX_A + a_{18}X_SX_M + a_{19}X_PX_A + a_{20}X_PX_M + a_{21}X_AX_M \end{aligned} \quad (3)$$

Here, y represents the response variables T_{gs}, K, E, B, T'_g, T'_m, w'_s. Parameters a_1–a_{21} are the coefficients from the regression model for the analysis of variance (ANOVA). A confidence level of 95% ($p < 0.05$) with MODDE 7.0 statistical software (Umetrics AB) was used. Equation (3) was reduced to its corresponding pruned forms after the omission of the statistically nonsignificant coefficient values ($p > 0.10$) and mathematical models were developed.

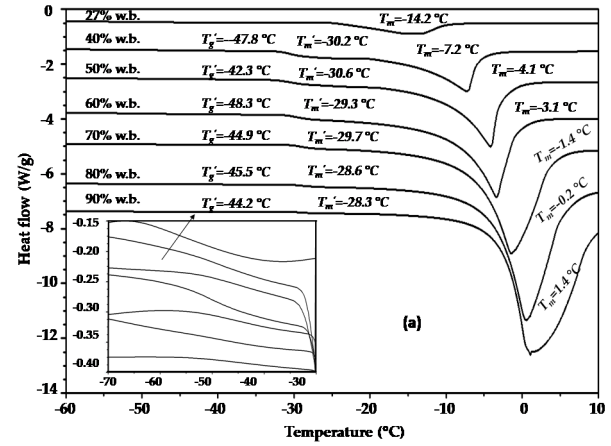
3. Results

3.1. DSC Thermograms

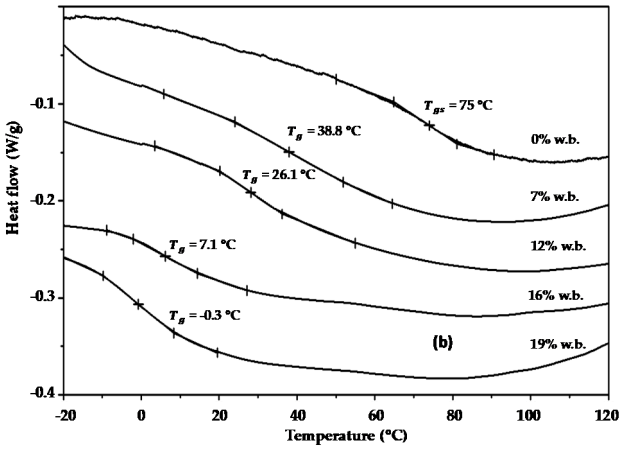
Figure 1a shows as an example the heating DSC thermograms obtained for the model food system with the chemical composition of $0.45X_F$:$0.15X_P$:$0.4X_M$ (experiment no. 6, Table 1) and prepared with moisture contents in the range of 27% to 90% wet basis (w.b.).

The thermograms show three thermal events in which the endothermic peak of ice melting was the most visible feature, preceded by two changes in the baseline, both with characteristics typical of a glass transition [11]. It can be observed that the T_m value was greatly depressed as the solid content was increased, ranging in this case from 1.4 to −14.2 °C. The melting point is defined as the temperature at which the liquid and solid phases of water at a given pressure are in equilibrium, while the presence of solutes increases the complexity of crystallization and reduces the partial pressure of water. Therefore, the equilibrium between the two phases (ice and water) can only be reached through a reduction in temperature [1,2,39]. It was also evident that the phase change peak becomes smaller as the solid content increases in the sample because of the reduction of the amount of freezable water in the samples. For aqueous sugar solutions, as in this case, it has been suggested that the first transition can be attributed to the glass transition of the maximally freeze-concentrated phase (T'_g), and the second transition can be considered as the beginning of the melting of ice crystals (T'_m) [40]. Figure 1a shows that the first transition was detected between −48.3 and −42.3 °C and the second one between −30.6 and −28.3 °C. Both parameters varied very little when the water content varied between 27% and 90%, as observed by Grajales-Lagunes et al. [4] and Ruiz-Cabrera et al. [22]. Therefore, the corresponding average values of T'_g and T'_m for each of the samples in Table 1 were estimated, reported, and subjected to statistical analysis using Equation (3), which are discussed later.

Figure 1b also shows as an example the reheating DSC thermograms obtained for the model food system with the chemical composition of $0.45X_s$:$0.15X_P$:$0.4X_M$ (experiment no. 8, Table 1) and prepared in the reduced moisture range of 0% to 19% w.b. It can be observed that the samples with any moisture content exhibited a clear endothermic shift because of the glass transition, with T_g values ranging from −0.3 °C to 75 °C. The T_g values became higher as the solid contents were increased in the samples because of the plasticizing effect of water on the glass transition temperature. It can also be seen in Figure 1b that glass transition occurred over a large temperature range (around 40 and 50 °C). These behaviors can be explained by the presence of maltodextrin in the samples. It is assumed that high molecular weight food components such as proteins, starches, and maltodextrin may exhibit glass transition with temperatures as high as 50 °C [2]. It is important to note, however, that good compatibility was achieved for the components, because global T_g values were observed in all the samples.



(**a**)



(**b**)

Figure 1. Differential scanning calorimetry (DSC) thermograms used for thermal analysis in model food systems: (**a**) the determination of T'_g, T'_m, and T_m in experiment no. 6 ($0.45X_F$:$0.15X_P$:$0.4X_M$) containing freezable water; (**b**) the determination of T_g in experiment no. 8 ($0.45X_S$:$0.15X_P$:$0.4X_M$) containing unfreezable water.

The heating DSC thermograms of the aqueous model systems of exp. nos. 4, 19, 6, 22, and 5 (Table 1) were chosen to illustrate the effects of the maltodextrin concentration on the T'_g, T'_m, and T_m values, as shown in Figure 2a. In this case, all the samples were prepared at the same moisture content of 60% w.b., whereas the maltodextrin mass fraction varied at intervals of approximately 0.2 in the concentration range of 0 to 0.8. As expected, the highest T_m value (0.8 °C) was obtained for the sample with the highest maltodextrin mass fraction (exp. no. 4), while the lowest T_m value (−6.6 °C) was obtained for the sample with no addition of maltodextrin (exp. no. 5). The freezing point depression is directly proportional to the molar concentration of a solution. This indicates that the lower the molecular mass of a solute, the higher the freezing point depression; that is, a high molecular weight substance has fewer molecules per gram than a low molecular weight one, which demonstrates fewer effects on the freezing point (T_m). Therefore, the depression in the freezing point decreased as the amount of maltodextrin was increased, as shown in Figure 2a. The same trend was observed for the T'_m values, which varied from −9.4 °C to −38.6 °C. This trend is to be expected, since T'_m represents the end point of freezing or the beginning of the melting of ice crystals [40]. The values obtained for T'_g, however, which ranged from −46.2 to −54.5 °C, did not highlight a clear tendency as occurred with T_m and T'_m values. In the literature, it has been reported that T'_m and T'_g depend strongly on the type and molecular weight of the food components [2,40]. Therefore, this suggests that other factors such

as compound interactions are also involved. Note that only one transition at −9.4 °C was observed for the sample of exp. no 4, and the value of T'_g, was not detected in this sample. These findings are similar to those of Flores-Ramírez et al. [11] and Roos and Karel [40], and are tentatively attributed to the overlapping of the glass transition with the ice melting caused by the HMW of maltodextrin.

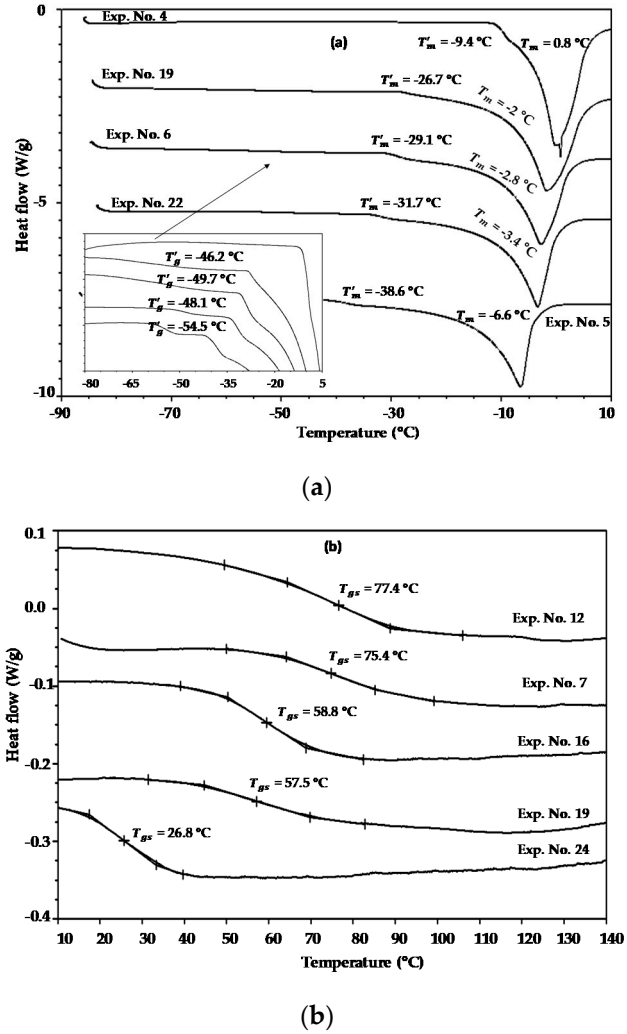
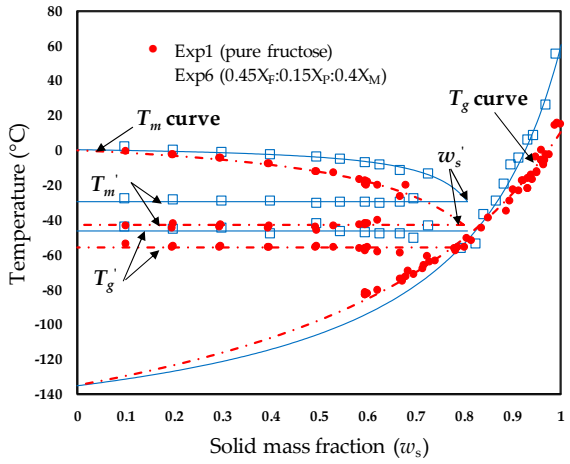


Figure 2. DSC thermograms used for thermal analysis in model food systems: (**a**) the effects of maltodextrin concentration on the T'_g, T'_m, and T_m values of samples prepared at 60% w.b.; (**b**) the effects of maltodextrin concentration on the T_{gs} values of anhydrous samples.

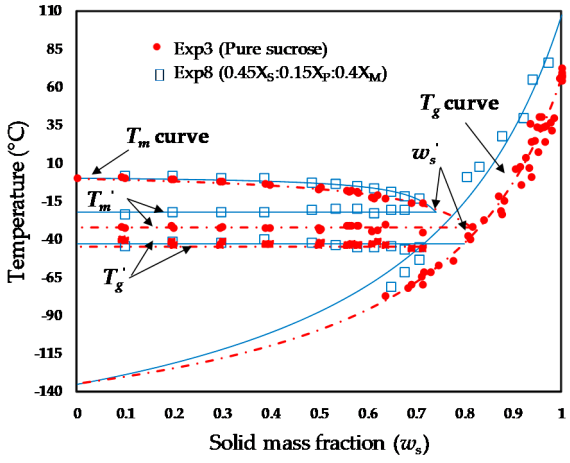
Because water plays a strong role in the T_g of foods and its value is very low (−135 °C), not taking into account its effect, the reheating DSC thermograms of the model systems of exp. nos. 12, 7, 16, 19, and 24 (Table 1) equilibrated over Drierite® were chosen to understand the effects of maltodextrin addition on the glass transition temperatures of anhydrous samples (T_{gs}), as shown in Figure 2b. In general, it can be established that all the model systems with added maltodextrin (exp. nos. 12, 7, 16, and 19) exhibited higher T_{gs} values than the model system without maltodextrin (exp. no. 24), which can be attributed to the high T_g value of the maltodextrin (170 to 180 °C) [40]. No proportional relationship between T_g and the maltodextrin concentration was observed, however, because no significant difference between the T_g values was found for the anhydrous samples of exp. no. 12 and exp. no. 7, nor for the samples of exp. no 16 and exp. no. 19 (Table 1). It is well established that the T_g values of amorphous materials are mainly affected by the molecular weight, chemical composition, and plasticizer [2,40]. Therefore, it is evident that the plasticizing effects of low molecular weight compounds such as glucose, fructose, and citric acid are also important in fruit juices [2].

3.2. State Diagrams

The experimental freezing points and glass transition temperatures measured by DSC were plotted as functions of the solid contents (w_s) in order to develop the state diagrams of each of the studied samples. As examples, a comparison of the state diagrams obtained for exp. no. 1 (pure fructose), exp. no. 6 ($0.45X_F$:$0.15X_P$:$0.4X_M$), exp. no. 3 (pure sucrose), and exp. no. 8 ($0.45X_s$:$0.15X_P$:$0.4X_M$) are respectively shown in Figure 3a,b.



(**a**)



(**b**)

Figure 3. Examples of state diagrams obtained for fruit juice model systems: (**a**) comparison of experiment no. 1 (pure fructose) and experiment no. 6 ($0.45X_F$:$0.15X_P$:$0.4X_M$); (**b**) comparison of experiment no. 3 (pure sucrose) and experiment no. 8 ($0.45X_s$:$0.15X_P$:$0.4X_M$).

As expected, a significant increase of the T'_g, T'_m, T_m, and T_g values was observed in the model food systems with added maltodextrin, and such effects can be better appreciated over the entire solid mass fraction scale, as shown in Figure 3. Generally, the predicted T_g curves with the G-T equation (Equation (1)) shifted upwards with increased maltodextrin content. In this way, the predicted T_{gs} values for pure fructose and pure sucrose were, respectively, 10.4 °C and 65.4 °C, whereas the corresponding values for the samples of exp. no. 6 and exp. o. 8, both with maltodextrin fractions of 0.4, were 60.3 °C and 107 °C, respectively (Table 2). The T_{gs} values estimated for fructose and sucrose were reasonably consistent with those reported in the literature for both sugars [2,41]. On the other hand, the predicted T_m curves with the Chen equation (Equation (2)) were less pronounced for the samples containing maltodextrin (exp. no. 6 and exp. no. 8), which always exhibited higher

T_m values in the freezable water domain. As previously mentioned, the freezing point depression is highly dependent on the molecular weight of the systems. This reduced freezing point depression may be relevant for industrial processes such as subcooling, in which the partial or total formation of ice crystals is achieved at relatively high temperatures (−4 °C), and thus the availability of water and water activity to slow microorganism growth is reduced. From Figure 3, it is also observed that the added maltodextrin exhibits a greater influence on the T'_m values than the T'_g values, because T'_m represents the end freezing point, which is also highly dependent on the molecular weights of the compounds, as previously discussed. In Figure 3, it can also be verified that both T'_g and T'_m exhibited little variation from the solid mass fraction; therefore, average values can be considered in these samples [4,22]. As a general trend, a proportional increase of the maltodextrin concentration was expected for the w'_s values, because the unfreezable water mass fraction ($w'_w = 1 - w'_s$) should be reduced as the solid content of maltodextrin is increased in the samples. Nevertheless, the opposite compositional dependence of w'_s has also been established for some samples, such as pure sucrose (Figure 3b, Table 2), which exhibited one of the highest values of w'_s (0.796 g solid/g sample). Therefore, an experimental method other than the intersection of the average value of T'_m with the T_m curve to accurately determine the maximum freeze concentration is required.

Table 2. Fitting parameters of Equations (1) and (2), and parameters of the maximal-freeze-concentration condition (MFCC).

Experiment	Parameters of Equation (1)			Parameters of Equation (2)			MFCC		
No.	T_{gs} (°C)	K	R^2	E	B	R^2	T'_g (°C)	T'_m (°C)	w'_s
1	10.4	2.90	0.986	0.0954	0.1668	0.991	−55.9	−42.8	0.739
2	31.8	3.79	0.994	0.1103	0.0557	0.968	−55.7	−41.8	0.783
3	65.2	4.68	0.975	0.0584	0.0980	0.964	−43.1	−32.5	0.796
4	157.3	10.32	0.808	0.0085	0.1595	0.929	−9.5	−9.5	0.801
5	25.6	3.33	0.990	0.0781	0.2178	0.991	−56.4	−38.7	0.716
6	60.3	5.59	0.983	0.0371	0.1280	0.971	−46.6	−29.6	0.807
7	61.6	5.75	0.964	0.0535	0.0741	0.974	−54.8	−30.2	0.812
8	107	4.09	0.970	0.0256	0.2442	0.975	−44.6	−22.3	0.741
9	24.7	3.53	0.981	0.0877	0.0697	0.950	−50.2	−38.4	0.791
10	41	3.85	0.984	0.0786	0.1076	0.971	−52.0	−38.8	0.781
11	19.1	3.52	0.976	0.0956	0.0936	0.972	−54.6	−42.6	0.781
12	64	6.12	0.876	0.0517	0.1399	0.969	−52.0	−32.0	0.780
13	16.4	3.73	0.954	0.0734	0.1958	0.987	−56.9	−39.3	0.738
14	34.4	4.04	0.987	0.0806	0.1805	0.987	−57.1	−39.0	0.737
15	46.6	4.16	0.951	0.0673	0.1340	0.974	−50.4	−34.7	0.768
16	37.7	4.18	0.899	0.0706	0.1770	0.983	−55.9	−36.9	0.746
17	66	5.44	0.904	0.0552	0.1953	0.966	−51.6	−34.8	0.750
18	73.5	6.41	0.890	0.0553	0.2107	0.988	−52.3	−34.4	0.740
19	47.6	5.06	0.884	0.0385	0.0770	0.967	−47.4	−25.5	0.824
20	52.4	4.43	0.963	0.0529	0.2970	0.986	−55.5	−36.1	0.702
21	67.1	6.09	0.886	0.0700	0.1644	0.985	−55.4	−36.5	0.752
22	92.4	6.90	0.971	0.0408	0.2569	0.981	−48.9	−31.6	0.730
23	18.8	3.75	0.949	0.0841	0.1467	0.985	−56.4	−38.6	0.751
24	36.6	3.43	0.976	0.0583	0.2462	0.984	−53.5	−35.1	0.719
25	54.2	4.78	0.965	0.0801	0.0865	0.977	−55.8	−35.3	0.780

The estimated parameters of the G-T equation (Equation (1)), the Chen equation (Equation (2)), and the maximal-freeze-concentration condition for each of the studied samples are shown in Table 2. From Table 2, it is observed that for the model systems the parameter ranges are as follows: T_{gs}:10.4 °C–157.3 °C; K: 2.90–10.32; E: 0.0085–0.1103; B: 0.0557–0.297; T'_g: −57.1 °C−−9.5 °C; T'_m:−42.8 °C−−9.5 °C; w'_s: 0.702–0.824 g solid/g sample, with R^2 values in the range 0.808–0.994. According to the data for several fruits, such as prickly pear cactus, orange, strawberry, pineapple, apple, date fruit,

raspberry, and blueberry, performed by Grajales-Lagunes et al. [4], these parameters varied as follows: T_{gs}:12.2 °C–74.6 °C; K: 3.02–5.72; E: 0.0178–0.238; B: 0.04–0.1657; T'_g: −58.8 °C–−46.4 °C; T'_m:−50.3 °C–−31.2 °C; w'_s: 0.690–0.847. The upper limits for the T_{gs} and K parameters obtained in this study are well above those reported in the aforementioned study, while the lower limit of the E parameter is lower. Similarly, the upper limits of the T'_g and T'_m values are also well above the values reported for model and real systems [4]. These differences can be mainly attributed to the maltodextrin presence in the systems.

The obtained mathematical models, the ANOVA, and the effect of each component on the T_{gs}, K, E, B, T'_g, T'_m, and w'_s values are given in Table 3. Equation (3) was used to interpret data variability with the determination coefficients, standard deviation, and coefficient of variation, respectively, in the ranges of 0.833–0.999, 0.00682–6.22, and 1.22–23.2. In addition, significance values varied between 0.2143 and <0.0001 (Table 3). From Table 3, it is observed that T_{gs}, K, E, B, T'_g, T'_m, and w'_s were all linearly affected by the mass fractions of the components, followed by binary interactions, with the parameters T'_g and w'_s being the most affected. Taking into account the regression coefficients of the models, it can be seen that pectin (X_P) and citric acid (X_A) are the most important variables affecting all parameters, while the interactions of maltodextrin (X_M) with the other components play important roles in the T'_m values, and the interactions of maltodextrin and pectin with other components have important effects on the parameter B. Regarding the ANOVA, it can be observed (Table 3) that all of the models are significant (P ($F > F_0$)), with the exception of the parameter w'_s, and there is a high probability that other factors not included in the model (noise) affect this response variable. The high values obtained for R^2 indicated that good control in the performance of the experiments and in the parameter determinations was achieved. On the other hand, the coefficients of variation shown in Table 3 generally indicated that there is homogeneity among the obtained data.

Table 3. Solute composition-based mathematical models and ANOVA ($p < 0.05$).

Model	ANOVA			
	P ($F > F_0$)	R^2	S. D.	C.V. (%)
$T_{gs} = 8.31X_F + 29.98X_G + 58.68X_S + 1295.36X_P - 885.31X_A + 10.52X_M - 2139.92X_FX_P + 1653.18X_FX_A - 2555.95X_GX_P + 2109.04X_GX_A + 122.3X_GX_M - 3002.49X_SX_P + 2526.09X_SX_A + 468.11X_SX_M$	<0.0001	0.983	6.22	11.86
$K = 2.9X_F + 3.76X_G + 4.48X_S - 130.1X_P + 119.4X_A + 3.59X_M + 109.55X_FX_P - 106.31X_FX_A + 72.36X_GX_P - 67.19X_GX_A + 12.55X_GX_M + 28.65X_SX_M + 119.8X_PX_A + 249.97X_PX_M - 248.14X_AX_M$	<0.0001	0.984	0.31	6.42
$E = 0.946X_F + 0.1019X_G + 0.0617X_S + 0.0543X_P + 0.0648X_A - 0.0003 - 0.1471X_FX_P - 0.0719X_SX_M$	<0.0001	0.94	0.00682	10.61
$B = 0.1413X_F + 0.0645X_G + 0.0956X_S - 9.0225X_P + 3.9767X_A - 0.0164X_M + 8.3373X_FX_P + 8.0965X_GX_P + 7.8839X_SX_P + 1.0128X_SX_M + 14.3016X_PX_M - 9.8217X_AX_M$	0.0018	0.833	0.04	23.25
$T'_g = -55.95X_F - 55.56X_G - 43.16X_S - 2063.09X_P + 1103.46X_A - 34.36X_M + 4.43X_FX_G - 1.41X_FX_S + 2027.37X_FX_P - 1249.55X_FX_A - 23.35X_FX_M - 11.19X_GX_S + 1899.63X_GX_P - 1130.07X_GX_A - 22.25X_GX_M + 1921.26X_SX_P - 1169.78X_SX_A - 4.93X_SX_M + 1987.27X_PX_A + 2819.84X_PX_M - 2024.59X_AX_M$	<0.0001	0.999	0.61	1.2
$T'_m = -42.92X_F - 42.31X_G - 33.39X_S - 72.78X_P + 13.8X_A - 10.8X_M - 17.99X_FX_M - 21.09X_GX_M - 15.8X_SX_A + 134.61X_PX_M - 172.4X_AX_M$	<0.0001	0.994	0.69	2.02
$w'_s = 0.75X_F + 0.78X_G + 0.80X_S + 51.35X_P - 36.73X_A + 0.72X_M + 0.08X_FX_G + 0.03X_FX_S - 53.72X_FX_P + 39.01X_FX_A + 0.05X_FX_M + 0.02X_GX_S - 52.92X_GX_P + 38.22X_GX_A - 0.30X_GX_M - 53.85X_SX_P + 39.16X_SX_A - 0.40X_SX_M - 19.73X_PX_A - 65.01X_PX_M + 57.76X_AX_M$	0.2143	0.921	0.02	2.94

P ($F > F_0$) = Fisher probability; S.D. = Standard deviation; C.V. = Coefficient of variation.

As an example, the performance of the empirical equations given in Table 3 can be observed in Figure 4, where a comparison between the predicted state diagrams at different maltodextrin mass fractions for the model food system $0.283X_F$:$0.283X_G$:$0.283X_S$:$0.075X_A$:$0.075X_P$ (experiment no.5, Table 1) was performed. The solid composition of experiment no. 5. was chosen because sucrose, fructose, glucose, pectin, and citric acid are the main solutes of fruit and vegetables, and the maltodextrin mass fraction in the sample was varied between 0 and 0.6. In this case, it was found that the higher the value of the maltodextrin mass fraction (X_M), the higher the values of T'_g, T'_m, and w'_s, and the less pronounced the curvature of the T_m curve. On the other hand, although the curvatures of the predicted T_g curves of samples containing maltodextrin were more pronounced compared with the sample without maltodextrin, no significant differences between the T_g curves were found when maltodextrin mass fractions of 0.3 and 0.6 were used. A dominant role of the T_g of amorphous mango

pulp at a higher maltodextrin weight fraction than 0.7 was also observed by Fongin et al. [38]. Perhaps this is one of the reasons why high concentrations of maltodextrins are used as carrier agents in spray drying processes. In this context, the solute-composition-based mathematical models resulting from this study are relevant for predicting state diagrams to monitor the progress and development of various processes, such as freezing, refrigeration, and drying.

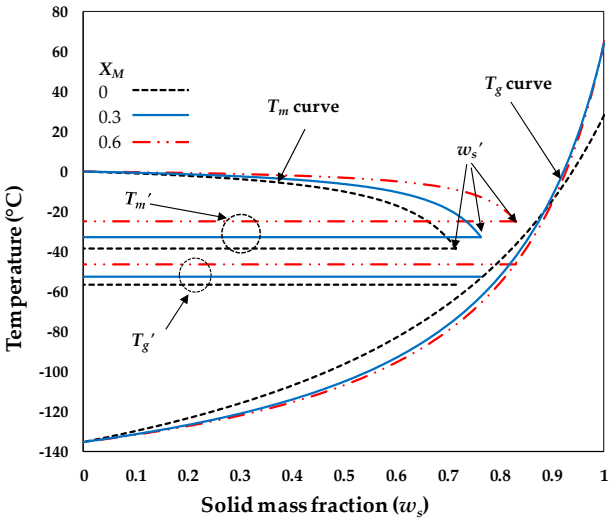


Figure 4. Influence of the maltodextrin mass fraction on the predicted state diagram for the fruit juice model system of experiment no. 5 using X_M = 0, 0.3 and 0.6.

4. Conclusions

The effects of maltodextrin addition on T'_g, T'_m, T_m, and T_g the during the construction of state diagrams of several fruit juice model systems were investigated. Increasing the maltodextrin mass fraction resulted in a significant increase of the abovementioned thermal transitions. Maltodextrin mass fractions higher than 0.4, however, are required to induce a significant increase of T'_g, T'_m, T_m, and T_g curves. Maltodextrin, therefore, can be considered as a good alternative in the formulation of cryoprotective media for adequate frozen preservation of high- and intermediate-moisture foodstuffs and as a carrier agent in the spray drying process. The developed mathematical models facilitated the determination of the influence of the chemical composition on the T_{gs}, K, E, B, T'_g, T'_m, and w'_s values, and could also be used to predict the state diagrams of samples as a function of the concentrations of solutes predominant in fruit juices and the maltodextrin weight fraction. In this context, the solute-composition-based mathematical models resulting from this study are relevant to the design and optimization of processes and storage procedures for fruit products in the low-, intermediate-, and high-moisture domains.

Author Contributions: P.G.-C. contributed to the concept of the study and carried out the experiments. A.F.-R. and C.G.-H. assisted with DSC measurements and sample preparation. R.G.-G. contributed to the experimental design and data analysis. A.G.-L. and M.A.-A. contributed to the interpretation of the results and the preparation of the manuscript. M.A.R.-C. contributed to the concept, the interpretation of the results, and the preparation of the manuscript. All authors have read and agreed to the published version of the manuscript.

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RESUMEN EN EXTENSO 3

Articulo enviado a la revista:

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Effect of maltodextrin weight fraction on the amorphous state and critical storage conditions of freeze-dried juices

Alma Flores-Ramírez, Alicia Grajales-Lagunes, Miguel Abud-Archila, Miguel A. Ruiz-Cabrera

INTRODUCCIÓN

Las frutas en polvo son uno de los productos más importantes en la industria alimentaria. Los procesos de deshidratación como el secado por aspersión, la liofilización, espumado combinado con convección y el secado por ventana refractante se utilizan generalmente para producir polvos a partir de jugos de fruta, los que generalmente se obtienen en estado amorfo (Fernández *et al*., 2011). Los materiales amorfos exhiben un volumen libre, entropía y niveles de energía más altos que sus contrapartes cristalinas, por lo que tienen una mayor solubilidad aparente y tasas de disociación más rápidas (Einfalt et al., 2013). Los polvos amorfos son sistemas en estado de no equilibrio y metaestable, tienen propiedades dependientes de la temperatura y la humedad mostrando una estabilidad física más baja en comparación con los polvos cristalinos. Como consecuencia los polvos de fruta son extremadamente higroscópicos y pueden sufrir una transición del estado vítreo al estado gomoso, promoviendo cambios físicos como apelmazamiento, colapso y cristalización de azúcares (Mosquera et al., 2012). Debido a que los polvos de frutas tienen valores bajos de T_g estando muy por debajo de las temperaturas típicas de almacenamiento (Syamaladevi *et al*., 2009). Los polímeros con alto peso molecular, de bajo costo y baja viscosidad a altas concentraciones de sólidos, tales como las maltodextrinas se han utilizado para elevar los valores de T_{gs} y en consecuencia la mejora de las condiciones de almacenamiento críticas de los polvos de frutas. García-Coronado et al (2020), reportan que usando una fracción másica de maltodextrina DE 4-7(X_{MD}) se incrementan las propiedades térmicas de T_g', T_m' y T_g.

OBJETIVOS

1. Evaluar el efecto de la fracción másica de maltodextrina con DE 4-7 (X_{MD}) sobre las isotermas de sorción de agua y la transición vítrea de jugos liofilizados de tuna, kiwi, fresa y piña.
2. Determinar las condiciones críticas de almacenamiento de jugos liofilizados de tuna, kiwi, fresa y piña basados en los valores T_{gs}, a_{WC} X_{WC}.

MATERIALES Y MÉTODOS

Cuatro frutas fueron elegidas para evaluar el efecto de la maltodextrina DE 4-7 sobre las condiciones de almacenamiento los sistemas reales. Para ello se obtuvieron los jugos de cada una de ellas (fresa, piña, kiwi y tuna). Los jugos se filtraron para eliminar los sólidos no solubles. Para conocer la composición de los sólidos solubles en los jugos de fruta se utilizó un HPLC Utimate 3000 Thermo Scientific. Así mismo se le determinó los grados °Brix con un refractómetro digital Leica, para conocer el contenido de sólidos solubles totales. En base al contenido de solidos se realizó un ajuste con la solución de maltodextrina al 40% y obtener fracciones másicas de 0, 0.4 y 0.8 de maltodextrina en los jugos de frutas. Posteriormente, las muestras fueron congelarlas a una temperatura de - 80 °C durante 24 horas para favorecer la formación de pequeños cristales de hielo y liofilizadas a -63°C y 5 mTorr. Una vez obtenidos los diferentes polvos se procedió a llevarlos a un equilibrio de actividad de agua de 0 durante un período de 6 semanas. Después de este tiempo se almacenaron los jugos a diferentes actividades de agua (0.14-0.91) con soluciones de sales saturadas (LiCl, CH_3COOK, K_2CO_3, Mg $(NO_3)_2$, NaCl, KCl y $BaCl_2$). Las diferentes muestras fueron pesadas cada 4 días hasta equilibrio constante. Después de este equilibrio se procedió a realizar el análisis calorimétrico de cada una de los jugos a las diferentes fracciones másicas y actividades de agua con la finalidad de determinar la temperatura de transición vítrea. La metodología calorimétrica consistió en dos calentamientos de la muestra el primero de ellos se llevó a cabo con la finalidad de fundir los cristales de los polvos y el segundo se realizó para determinar el valor de T_g. Una vez obtenidos cada uno de estos parámetros se procedió a la modulación de la temperatura de transición vítrea mediante una ecuación polinómica y la modelación de la isoterma desorción mediante el modelo de GAB para así obtener los diagramas de estado simplificados para los jugos de piña fresa kiwi y tuna con y sin la adición de maltodextrina y conocer las condiciones críticas de almacenamiento.

RESULTADOS

Dado que los solutos presentes en los jugos de fruta tienen una influencia sobre el valor de T_g, fue necesario conocer la concentración de glucosa, sacarosa, fructosa, ácido cítrico y pectina de cada jugo. Se encontró que el kiwi presenta mayor concentración de fructosa, la tuna presento concentraciones más altas de glucosa y la concentración más alta de sacarosa la presento el jugo de piña. Por otra parte, se obtuvieron los diagramas de estado que combinan la transición vítrea y las isotermas de sorción de jugos de frutas liofilizados adicionados con fracciones másicas de maltodextrina de 0, 0.4 y 0.8. El aumento gradual de X_w se atribuye al efecto predominante de las interacciones soluto-solvente y la disolución del soluto, mientras que la disminución de T_g se asocia con el efecto plastificante del agua. Los valores de T_g y X_w de los polvos que contenían maltodextrina, independientemente del valor de a_w, fue mayor que el de los polvos de jugo puros, este aumento fue mayor en los jugos de piña con maltodextrina, este aumento se pudo deber a la mayor presencia de sacarosa. Indicando que el aumento de a_{WC} y X_{WC} es dependiente de la composición de los jugos de fruta. Cuanto mayor sea el valor de X_{MD}, mayor será el efecto esperado sobre estas propiedades. Los jugos en polvo anhidros proporcionaron valores de T_{gs} que variaron de 28.5 ± 1.0 a 110.5 ± 1.6 °C, mientras que los valores mínimos se presentaron en los polvos de jugos naturales y los más altos en los polvos preparados con maltodextrina con X_{MD} de 0.8. Puede verse que a_{WC} y X_{WC} para el polvo de fresa variaron, de 0.078 a 0.590 y 0.024 a 0.137 (b. s.), para piña en polvo de 0,174 a 0,632 y de 0,029 a 0,142 (b. s.), para kiwi en polvo de 0,029 a 0,550 y de 0,013 a 0,129 (b. s.) y para tuna en polvo de 0,077 a 0,570 y de 0,017 a 0,120 (b. s.), respectivamente. Se encontró que los valores críticos de los polvos de jugo natural y los polvos que contienen maltodextrina de este estudio están en los rangos reportados en la literatura. Las características reveladas en los polvos almacenados a los diferentes actividades de agua son las siguientes: todos los polvos permanecieron inalterados por debajo de los valores de aw correspondiente; se obtuvieron polvos en estado amorfo hasta una aw de 0.52 con X_{MD} de 0.8; se

observó disolución de solutos y pardeamiento no enzimático en todas las muestras a aw superiores a 0.75.

CONCLUSIÓN

Los diagramas de estados de los polvos se describieron mediante modelos polinomiales y la ecuación de GAB. El aumento del valor de X_{MD} de 0 a 0,8 reportó un aumento significativo de los valores críticos. Los resultados también muestran que a_{WC} y X_{WC} de las muestras dependen del tipo de sólido presente en los jugos ($p < 0.05$). Los valores críticos más altos se encontraron en los polvos de piña que van desde 0.174–0.632 y 0.029–0.142 (b. s.) y los más bajos en los jugos de kiwi en polvo, que van desde 0.029–0.550 y 0.013–0.129 (b. s.). Por encima de X_{MD} de 0,8, independientemente de la composición del jugo, todos los polvos tienden a tener el mismo valor de a_{wc}. Se demostró la idoneidad de a_{WC} definido con a_{WC} experimental para predecir la estabilidad de los polvos a 25 °C. Además, a 25 °C, todos los polvos preparados con X_{MD} de 0,8 fueron amorfos y estables hasta un a_{WC} de 0.52.

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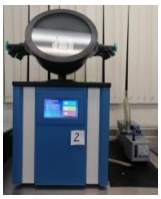
RESUMEN GRÁFICO 3

X_M=0 X_M=0.4 X_M=0.8

Jugos de frutas acondicionados



T=-63°C
P=5mtorr

t=6 semanas
T=25°C

Análisis calorimétrico

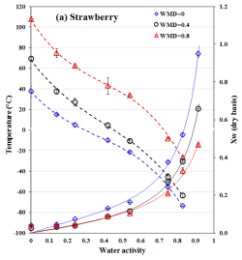
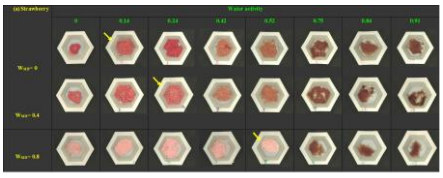


Diagrama de estado



Condiciones criticas de almacenamiento

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Effect of maltodextrin weight fraction on the amorphous state and critical storage conditions of freeze-dried juices

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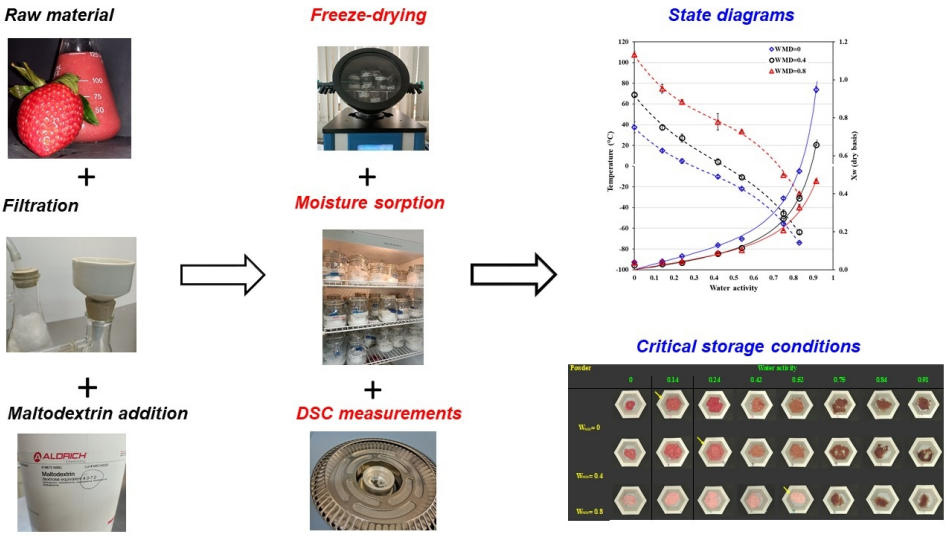
Keywords:	State diagram, fruit juice powders, glass transition, maltodextrin, storage stability



355x200mm (96 x 96 DPI)

Effect of maltodextrin weight fraction on the amorphous state and critical storage conditions of freeze-dried juices

Alma Flores-Ramírez[1], Alicia Grajales-Lagunes[1], Miguel Abud-Archila[2], Miguel A. Ruiz-Cabrera[1,*]

1 Faculty of Chemical Science. University of San Luis Potosi. 6 Dr Manuel Nava Avenue, University Area, San Luis Potosí, 78210, Mexico.

2 National Institute of Technology of Mexico. Technological Institute of Tuxtla Gutiérrez. Street km 1080, Tuxtla Gutiérrez, 29050, Mexico.

*Corresponding author e-mail: mruiz@uaslp.mx

Summary

State diagrams relating to water activity (a_w), equilibrium moisture content (X_w), and glass transition temperature (T_g) are valuable tools for predicting amorphous fruit powders' storage procedure and stability. Thus, state diagrams were constructed to characterise the amorphous state and define the critical values of water content (X_{wc}) and water activity (a_{wc}) of freeze-dried juices of strawberry, pineapple, kiwi and prickly pear prepared with maltodextrin at the dry mass fraction (W_{MD}) of 0, 0.4 and 0.8. T_g and sorption data were fitted with a polynomial equation and the GAB model, respectively (R^2>0.982). A Tukey test was performed to evaluate the difference between critical values of the powders ($p<0.05$). The a_{wc} and X_{wc} increase with W_{MD} and depend on the solid types of juices. The highest critical values were found in pineapple powders, ranging from 0.174 to 0.632 and 0.029 to 0.142 (dry basis), and the lowest ones in kiwi juice powders ranging from 0.029 to 0.550 and 0.013 to 0.129 (dry basis). For W_{MD} of 0.8, however, regardless of juice composition, stable powders in an amorphous state were obtained up to an a_w of 0.52 at 25°C.

Keywords: state diagrams, fruit juice powders, glass transition, maltodextrin, storage stability

CONCLUSIONES GENERALES

1 Los valores de T_g', T_m' y T_m aumentaron con respecto al peso molecular de crioprotector. El análisis estadístico de los datos ($p<0.05$) demostró que tanto la composición del soluto como del agua deben considerarse en la formulación de medios crioprotectores, ya que afectan significativamente los valores de T_g', T_m' y T_m ($p<0.05$).

2 Expresiones matemáticas para T_g', T_m' y T_m en función de las fracciones másicas de crioprotectores y agua y sus interacciones se desarrollaron para guiar la formulación de medios crioprotectores que involucran mezclas de más de dos crioprotectores para mejorar la estabilidad de almacenamiento y la calidad de productos alimenticios congelados con contenidos de humedad altos e intermedios con modificables formulaciones, como helados, purés, mermeladas, surimi, etc.

3 Se requieren fracciones másicas de maltodextrina superiores a 0.4 para inducir un aumento significativo de las curvas de T_g', T_m', T_m y T_g. Considerándose a la maltodextrina como alternativa en la formulación de medios crioprotectores para la adecuada conservación en congelado de productos alimenticios de humedad alta e intermedia y como agente acarreador en el proceso de secado por aspersión.

4 El desarrollo de modelos matemáticos facilitó la determinación de la influencia de la composición química en los valores de Tgs, K, B, T_g, T_m' y x_w', pudiendo predecir los diagramas de estado de muestras en función de las concentraciones de los solutos predominantes en jugos de frutas y la fracción de pesos de maltodextrina (DE 4-7).

5 La adición de fracciones másicas de maltodextrina (DE 4-7) de 0.4 o de 0.8 b.s a sistemas reales liofilizados (jugos de piña, fresa, tuna y kiwi) aumentan significativamente los valores de a_{wc}, La composición química de los polvos influye sobre los valores críticos, ya que la piña al contener mayor proporción de sacarosa en su composición presentó mayores valores de a_{wc} a una fracción másica de maltodextrina (DE 4-7) de 0.4. En fracciones másicas de 0.8 independiente de la composición todos los jugos presentan valores muy similares.