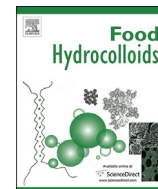




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FTIR spectroscopic evaluation of sucrose-maltodextrin-sodium citrate bioglass

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ABSTRACT

A model bioglass system was composed with sucrose (SC), maltodextrin (MD), and sodium citrate (NaCit). Samples were prepared with different SC/MD ratios (7:3, 5:5 and 3:7, by mass) and NaCit/SC ratios (0, 0.1 and 0.2, by mole) at low (0.27–0.49 %wb) and high (2.83–4.4 %wb) levels of moisture content. The effects of system constituents were investigated using the Fourier transform infrared (FTIR) spectroscopy. Hydrogen bonding interactions analyzed by studying the OH-stretching absorption band in the FTIR spectra indicated that there was no noticeable effect of moisture on the bioglass. The matrix of the system with high concentration of MD was loosely packed. NaCit interacted with both SC and MD through carboxylic groups, as evidenced by the shifting of antisymmetric ($\nu_{as}(\text{COO}^-)$) and symmetric ($\nu_s(\text{COO}^-)$) stretching bands of carboxyl groups. However, NaCit tended to interact more strongly with SC rather than with MD as evidenced by the strongest hydrogen-bonded network observed in the system with highest concentrations of SC (i.e., SC/MD = 7:3) and NaCit (i.e., NaCit/SC = 0.2).

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1. Introduction

Sucrose (SC) and maltodextrin (MD) are common ingredients found in various commercial food products. SC can be readily vitrified and has the ability to form hydrogen bonding with different other molecules. MD has a higher glass transition temperature (T_g) than SC, and it can inhibit crystallization. This ability of SC could be of prime importance for the stabilization of polymers in amorphous SC matrix (Davidson & Sun, 2001; Taylor & Zografis, 1998; Wolkers, van Kilsdonk, & Hoekstra, 1998). The utilization of sugar glasses as an encapsulation matrix could be enhanced by mixing with larger biomolecules such as (MD); this combination could also contribute to certain desirable characteristics. In spray drying, for example, an ideal carrier should have a high degree of solubility, limited viscosity at 30–45% solid content, emulsifying characteristics, good drying properties, bland taste, and non-reactivity. MD serves well for these purposes (Desobry, Netto, & Labuza, 1999; Galmarini, Zamora, Baby, Chirife, & Mesina, 2008). In addition, MD has proven to inhibit crystallization in amorphous SC matrix and provide good product stability to dry powder

products (Bhandari & Hartel, 2005). It was also found that glasses which is formulated from the mixtures of SC and MD exhibit stronger hydrogen bonding than pure SC glasses (Oldenhof, Wolkers, Fonseca, Passot, & Marin, 2005). Other interesting functional properties of MD are the ability to bind flavors and fat, and to serve as oxygen barrier (Chronakis, 1998).

It has been reported that salts have the potential to enhance the stability of sugar glasses when residual moisture is less than 2%. It was suggested that the mechanisms that help improve matrix stability are interactions between either ions (You & Ludescher, 2008b) or the functional groups (Kets, Ijpelaar, Hoekstra, & Vromans, 2004) of salts and sugar molecules. Sodium citrate (NaCit) is among the salts that has been of much interest to researchers. This type of salt is widely used in food products for various purposes. Based on these, we investigated if the addition of salt to a complex amorphous carbohydrate system (SC-MD) at low level of moisture content will significantly affect its glass transition properties (Sritham & Gunasekaran, 2016).

Fourier transform infrared (FTIR) spectroscopy is a powerful tool that facilitates the study of materials in amorphous state. The technique allows monitoring the changes in various chemical bonding species in the amorphous matrix. Many groups of researchers have employed the FTIR spectroscopy as a primary tool

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(Imamura et al., 2006; Ottenhof, MacNaughtan, & Farhat, 2003; Wolkers, Oldenhof, Alberda, & Hoekstra, 1998; Wolkers, Oliver, Tablin, & Crowe, 2004) while others used the technique as a complementary measurement to help interpret the results along with other techniques (Kadoya et al., 2008; Kets et al., 2004).

Among various absorption bands present in FTIR spectra, the hydroxyl (OH)-stretching vibration is the most useful for the study of amorphous carbohydrates. The length and the strength of intermolecular hydrogen bonding could be respectively inferred from the band position and the shift in band position of the OH-stretching vibration from FTIR spectra (Wolkers, Oliver, et al., 2004). Hydroxyl groups usually do not exist in isolation. They exhibit a high degree of association as a result of extensive hydrogen bonding. The interactions among these hydroxyl groups may be within the same molecule – intramolecular hydrogen bonding, or exist between neighboring molecules – intermolecular hydrogen bonding (Coates, 2000).

In a carbohydrate-water system, where water significantly contributes to OH-stretching absorption band, clusters of water molecules could be categorized into three families according to their hydrogen bond organization. The first, originating from tetrahedrally bonded water molecules, namely networking water, locates in the region of around 3300 to 3314 cm^{-1} . The second is intermediate water, which is a weakly or distorted hydrogen-bonded family locates at around 3441 to 3470 cm^{-1} . The last family is free or multimer water, which originates at around 3570 to 3610 cm^{-1} from water monomers and dimers and locates (Gallina, Sassi, Paolantoni, Morresi, & Cataliotti, 2006; Lerbret et al., 2005; Malsam & Aksan, 2009). The OH-bending absorption band which locates in the region of 1500 – 1800 cm^{-1} does not contain any contribution from the hydroxyl groups of carbohydrates; the band solely originates from water (Gallina et al., 2006; Lerbret et al., 2005; Malsam & Aksan, 2009). This region of 1500 to 800 cm^{-1} , the so called a “fingerprint” region of sugar, can be used to differentiate types of sugar according to their molecular vibration sensitivity to the flexibility around the glycosidic bond. Vibrations in this region are mainly attributed to in-ring CO-stretching, inter-ring COC-, COH- and CCH- bending, and symmetrical deformations of CH₂ groups. The fingerprint region is sensitive to a physical state (amorphous/crystalline, glassy/rubbery) of sugar and hence could be used to monitor the transitions between states (Ottenhof et al., 2003). The spectra next from the fingerprint region, in the range of 1800 to 1600 cm^{-1} , which usually arise from HOH-bending of water molecules, could provide important information about the effects of sugar on the hydrogen-bonded network of water (Gharsallaoui, Rogé, & Mathlouthi, 2008).

There exists a relationship between the rate of change of vibrational energy with temperature (wavenumber temperature coefficient, WTC) of OH-stretching vibration, and the glass transition of carbohydrate systems. The WTC is a parameter for determining the strength of hydrogen-bonded network. Typically, OH-stretching band falls in the range of 3200 – 3600 cm^{-1} , depending on temperature. As temperature rises, the band position of OH-stretching vibration shifts to the higher wavenumbers indicating the weakening of hydrogen bonds. An abrupt change in WTC of the OH-stretching mode has been observed during glass transition of carbohydrate systems. In fact, the OH-bending vibration also appears to relate to glass transition. However, this band falls in the fingerprint region of infrared (IR) spectrum, which is complex; many absorption bands with different temperature dependencies overlap in this region, and hence the assignment of this band becomes problematic.

Another evidence to confirm the applicability of IR spectroscopy for determining glass transition temperature (T_g) is the plasticizing effect of water on a sugar glass in that the highest value of T_g

determined with this technique was found in the sample with the lowest water content. There is however a limit for using the infrared (IR) spectroscopy for the analysis of T_g and WTC. As mentioned above, the OH-stretching vibration bands of water and sugar are superimposed leaving the technique applicable only to the systems with $0.3\text{ g H}_2\text{O/g}$ (dry weight) or lower (Wolkers, Oldenhof, et al., 1998).

From the studies on amorphous carbohydrates with different chain lengths, the results from FTIR analyses reveal interesting relationships among the characteristics of hydrogen bonding, T_g , and change in heat capacity during glass transition ($\Delta C_{p,GT}$). Wolkers, Oldenhof et al. (1998) reported a positive correlation between OH-stretching band position and T_g , which indicates that T_g increases with the average length of hydrogen bonds in amorphous sugars. The thermotropic response of OH-stretching vibration in the amorphous matrix revealed a relationship in which sugars with higher T_g exhibit greater degree of freedom to rearrange hydrogen bonds. Also, this higher degree of freedom to rearrange the molecular packing during temperature change helps to stabilize the amorphous matrix. Even though T_g of disaccharides generally shows a positive correlation with molecular weight, predicting the T_g of disaccharides based solely on molecular weight is inaccurate. Disaccharides exhibit a broad range of T_g : $70\text{ }^\circ\text{C}$ for dry SC, $95\text{ }^\circ\text{C}$ for dry maltose, and $110\text{ }^\circ\text{C}$ for trehalose. This wide distribution of T_g for disaccharides is believed to be an attribute of the differences in molecular packing, which may be associated with the differences in intermolecular hydrogen bonding. These differences are reflected in the band position and the thermotropic response of OH-stretching vibration.

As compared to SC, the WTC of OH-stretching vibration in a glassy state (WTC_g) of trehalose is higher. The higher WTC_g means the looser molecular packing. Thus carbohydrates that exhibit high T_g would possess a loose amorphous structure. Accordingly, the WTC_g is suggested as a measure for the degree of order or entropy in glassy state. It was also found that change in specific heat capacity at glass transition ($\Delta C_{p,GT}$) decreased with the increasing T_g , and so the increasing WTC_g. The finding indicates a direct association between $\Delta C_{p,GT}$ and the strength of hydrogen-bonded network of glassy systems (Wolkers, Oliver, et al., 2004).

Wolkers, Oliver, et al. (2004) studied the preservative property of sugars (glucose and SC) and phosphate systems on dried liposomes. FTIR measurements were carried out to investigate the interactions among phosphate, sugars, and egg phosphatidylcholine (egg PC) liposomes through hydrogen bonding, and to determine the T_g of the mixtures. The results show that the band position of OH-stretching vibration of sugars decreased with the increasing amount of phosphate and reached a minimum when phosphate/glucose ratio equal to unity. It was interpreted as phosphate contributes to increase, to a certain extent, the T_g of amorphous sugar matrices by forming strong hydrogen bonding. This effect could help stabilize the liposomes during air drying. The observation on the response of OH-stretching vibration suggested that liposomes also interacted with sugar through hydrogen bonding, but to a less extent than that between phosphate and sugar. Besides, it was found phosphate decreased the WTC of OH-stretching vibration in the glassy state, which means there was less degree of freedom for hydrogen bonds to rearrange themselves. As a result, it was speculated that the effects of phosphate could explain the poor storage ability of liposomes in sugar-phosphate glass even with elevated T_g (Wolkers, Oldenhof, Tablin, & Crowe, 2004).

The above results clearly demonstrate the significance of hydrogen bonding on the protective property of carbohydrate-glass systems. It should be noted, however, that the contribution of hydrogen bond networks to the amorphous matrix could be altered by a number of factors, e.g., molecular structure, molecular weight,

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