International Food Research Journal 23(4): 1700-1705 (2016)
Journal homepage: http://www.ifrj.upm.edu.my

Insight into the property and behavior of saccharides in amorphous state

[1]Sritham, E. and [2*]Gunasekaran, S.

[1]*Department of Food Engineering, Faculty of Engineering, King Mongkut's Institute of Technology Ladkrabang, Bangkok 10520 Thailand*
[2]*Department of Biological Systems Engineering, University of Wisconsin-Madison, Madison, WI 53706 USA*

Article history

Received: 1 July 2015
Received in revised form: 31 January 2016
Accepted: 9 February 2016

Keywords

Saccharide
Maltodextrin
Sucrose
Amorphous
T_g
Mechanical behavior

Abstract

This study was aimed at investigating the calorimetric property and the mechanical behavior of amorphous saccharide system. A mixture of sucrose and maltodextrin was chosen as a model system. The mixtures were formulated with three different sucrose/maltodextrin (SC/MD) ratios. It was found that the T_g increased with increasing maltodextrin concentration. Within the range of moisture content less than 4%, the average values of mid-T_g were 73, 80 and 105ºC for the systems with SC/MD of 7/3, 5/5 and 3/7, respectively. A strong plasticization effect of water on T_g was also observed. A difference in mechanical behavior for large- and small-molecular weight saccharides was revealed with the small strain oscillatory shear test. Maltodextrin (large-molecular weight saccharide) contributed to an elastic or solid-like characteristic, which suggests that the molecular motions are primarily involved in stretching and bending of glycosidic linkages. The large number of strong glycosidic linkages present in maltodextrin might be responsible for the high rigidity of the system. In contrast, sucrose (small-molecular weight saccharide) contributed to a viscous or liquid-like characteristic. The findings suggest that type and number density of glycosidic linkages significantly define the mechanical behavior of amorphous saccharide systems.

Introduction

In certain class of materials an enormous increase in viscosity during rapid cooling could prevent their molecules to rearrange themselves into a crystal lattice. This phenomenon introduces a material into an amorphous state. The amorphous state is thermodynamically out-of-equilibrium, and depending on temperature the amorphous materials exist either as a highly viscous supercooled liquid, rubbery, or glassy solid (Elliott *et al*., 1986; Allen, 1993). The molecular disorder of a glass is characteristic of its liquid state. Molecular motions remaining in glass are only vibrational and limited rotational. Rubbery solids and supercooled liquids exhibit macroscopic flow due to the onset of translational motion (Zallen, 1983). A number of common food processes such as drying, freezing, grinding, extrusion etc. yield amorphous or partially amorphous products (Liu *et al*., 2007). Information on properties and behavior of amorphous food materials is of crucial importance in food processing, handling and product development. This study was aimed to gain better understanding about some characteristics of glass transition and mechanical behavior of amorphous saccharides. The saccharide model systems were formulated with sucrose, a small molecular weight saccharide, and maltodextrin, a large molecular weight saccharide.

Materials and Methods

Sample preparation

Crystalline sucrose and maltodextrin powder (DE20) were respectively purchased from Fisher Scientific (Fair Lawn, NJ) and Spectrum Chemical Manufacturing Corporation (Gardena, CA) and used as received. Samples were formulated with three different sucrose/maltodextrin mass ratios (SC/MD): 7/3, 5/5 and 3/7. Sucrose-maltodextrin mixtures were dissolved with deionized water and stirred for 3 h. The sample solutions were then gradually heated from 145ºC up to 175ºC, stirring continuously, to obtain a molten mass with ~9% moisture content (wb). The samples were further prepared differently for calorimetric measurements and mechanical tests. For mechanical tests, the samples were formed into 5-mm diameter cylinders using a Teflon mold coated with paraffin oil. Molded samples were transferred into small glass tubes, vacuum-sealed in

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*Corresponding author.
Email: *guna@wisc.edu*

FoodSaver® plastic bags, and stored in a desiccator. For calorimetric measurements, the samples were spread over a flat Teflon surface, which allowed them to rapidly cool down to room temperature, and were transferred to a desiccator before grinding. Samples were ground and sieved through a 170-mesh screen. The ground samples were equilibrated in the atmosphere of P_2O_5 powder (Low RH) and saturated LiCl solution (High RH) to obtain two different moisture contents. Moisture contents were measured using Volumetric Karl Fischer titrator - model 795 KFT Titrino (Metrohm Ltd., Herisau, Switzerland) at 50ºC. At least two measurements were carried out for each sample. All treatments were prepared in duplicates.

Calorimetric measurements

The measurements were made using a modulated differential scanning calorimeter (MDSC, Model 2920, TA Instruments, New Castle, DE) equipped with a refrigerated cooling system. Nitrogen was used as a purge gas and as a cooling medium at the flow rates of 35 and 150 mL/min, respectively. As suggested in a previous study, a heating rate of 10ºC/min was selected (Angell, 1997), while the cooling rate used was 15ºC/min. Temperature and heat flow calibrations were performed using indium, tin, and distilled water. Temperature modulation amplitude was ±1ºC with a period of 60 s.

Samples were filled and tightly sealed in hermetic aluminum pans and lids. The filling was done within a glove box flushed with nitrogen. Mass of samples was in a range of 10 - 17 mg. A sealed empty pan was used as a reference. Two cycles of heating and cooling temperature scans, over the range of approximately 40ºC below the onset-T_g up to approximately 40ºC above the offset-T_g of each sample, were applied. The first cycle was intended to erase thermal history. The values of T_g were determined from a reversing heat flow signal of the second cycle. The locations of T_g values are graphically illustrated in Figure 1. At least three separate measurements were made on each sample.

Small strain oscillatory shear tests (SAOS)

Samples were removed from packages and cut into 5-mm diameter and about 7.56 ± 0.11 mm long cylindrical specimens. SAOS tests were conducted using a dynamic rheometer (Bohlin C-VOR, Malvern Inc., Southampton, MA) using a 20-mm, parallel-plate geometry (PP20). Cyanoacrylate adhesive was applied to affix specimens to the parallel plates. To minimize moisture absorption by the sample from the surroundings, a solvent trap was used; in addition, paraffin oil was applied all around the trap. Specimens were allowed to dry for 15 min. The tests were conducted isothermally at 25ºC in the frequency range of 0.01 – 150 Hz with the shear strain of 0.002%. Experimental data in rheological format were exported to MS Excel, manually corrected with the specimen geometry, and reported.

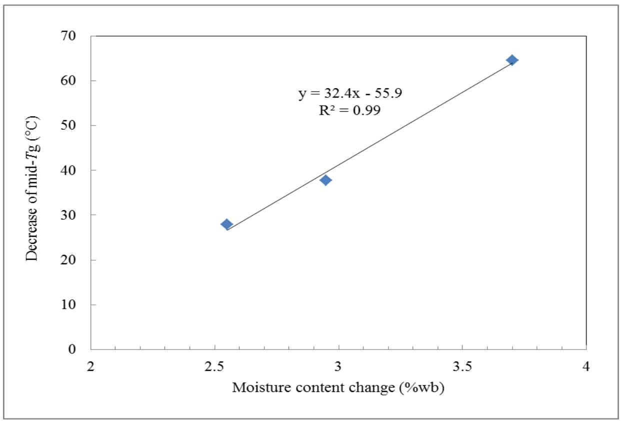

Figure 1. The plasticization effect of water in suppressing the T_g of amorphous saccharide mixture systems

Results and Discussion

Glass transition temperature

A calorimetric glass transition temperature can be defined in several ways. The most commonly reported values in literature are the mid-T_g (see also Figure1). In this study, however, we reported onset-, mid-, and offset-T_g values. The assignment of T_g can be found elsewhere (Icoz and Kokini, 2009). From the results given in Table 1, it can be seen that T_g clearly is depended on SC/MD. Samples formulated with the greater maltodextrin concentration exhibited the higher T_g. The size and complexity of glass forming molecules are among the factors which greatly affect T_g (Orford *et al*., 1990). Our results confirm that the larger and more complex the saccharide molecules – maltodextrin in this case – the higher the T_g value. Nevertheless, the observed T_g values are not solely influenced by of glass-forming molecules since the final moisture contents of different SC/MD samples were different. The T_g values of samples with higher maltodextrin concentration were greater even though their moisture contents were higher. Thus, we presume that, if all samples were of the same moisture content, the expected T_g values for the sample with higher maltodextrin concentration would be even greater.

The methods used in this study could bring the final moisture content of samples down to approximately 0.32 and 3.39% (wb) for Low and High levels, respectively (Table 1). It is well documented that water present in biological materials could act as a strong plasticizer and greatly suppress the T_g (Liu

Table 1. Glass transition data of amorphous sucrose-maltodextrin systems at two different levels of moisture content

Moisture Content levels	SC/MD	Moisture content (%wb)	T_g (°C)			Width of Glass Transition (°C)
			Onset	Mid	Offset	
Low	7/3	0.28±0.01	79.3±0.3	86.6±0.3	93.5±0.4	14.2±0.7
	5/5	0.34±0.03	89.1±1.6	99.2±1.8	110.5±1.1	21.3±0.6
	3/7	0.34±0.11	123.4±1.2	136.9±0.8	146.4±0.4	22.9±0.8
High	7/3	2.83±0.11	53.2±0.1	58.7±0.2	62.5±0.1	9.3±0.2
	5/5	3.29±0.02	55.8±0.3	61.4±0.2	65.2±0.1	9.5±0.2
	3/7	4.04±0.03	64.4±6.6	72.3±5.3	77.0±7.0	12.6±0.4

Remarks: The figure represents mean value ± standard deviation. The width of glass transition was determined based on the mid-T_g.

et al., 2006). Our results clearly show the effect of water molecules on the T_g values of every sample. A dramatic decrease in T_g (up to approximately 65ºC for the sample formulated with SC/MD of 3/7) was observed when moisture content increased by only a few percentages.

To investigate this further, the increase in moisture content was plotted against T_g suppression, which exhibited a linear relationship (Figure 1). T_g depression increased linearly with the increase in moisture content regardless of the composition. This implies that, within the range of moisture contents studied, water molecules affect the T_g of large and small saccharide molecules by a similar magnitude. However, Noel *et al*. (2000) reported that the more complex glass-forming molecules, the stronger the plasticization effect of water. Kilburn *et al*. (2004) proposed two possible mechanisms of plasticization by water molecules: the formation and disruption of intermolecular hydrogen bonds among carbohydrates, and the changes of free volume in the matrix. Water may either fill up small voids and/or disrupt intermolecular hydrogen bonds leading to a higher degree of freedom of the amorphous matrix (Liu *et al*., 2006).

Effect of water on glass transition width

The width of glass transition region (ΔT_g) is strongly correlated with the entropy production at the glass transition temperature. (Schmelzer and Tropin, 2013). The Moynihan correlation suggests that the activation energy of structural relaxation is inversely proportional to ΔT_g. This correlation is could be greatly helpful in that it allows the characterization of glass dynamic from a simple single measurement (Pikal *et al*., 2004). Heating and cooling rates could directly affect ΔT_g. In this study, the influence of heating and cooling rates on ΔT_g could be excluded since the setting was fixed for the entire experiments. It was found that the ΔT_g narrowed with the increasing moisture content (Table 1). Though no further analysis was performed, the result would indicate a noticeable effect of water on glass transition dynamic of amorphous saccharide system.

Mechanical behavior

Mechanical tests required samples with certain level of flexibility. Accordingly, samples were prepared with moisture contents ranging from approximately 8.5 to 10.5% (wb) so that the T_g was substantially suppressed and the samples were rubbery at room temperature. There appeared a positive correlation between moisture content of samples and maltodextrin concentration. It was noticeable that at the very last state of heat evaporation, the sample with higher maltodextrin concentration exhibited higher viscosity. The large glucose polymers with a broad spectrum of chain lengths and molecular weights in maltodextrin (McPherson and Seib, 1997; Chronakis, 1998) might be responsible for the increase in viscosity. The increased viscosity would then limit the attainable moisture content. Besides, the three-dimensional network of glucose polymers might contribute to a high degree the water holding capacity (Radosta *et al*., 1989a; Radosta *et al*., 1989b; Radosta and Schierbaum, 1990).

Representative dynamic mechanical spectra for the rubbery amorphous of saccharide mixtures are given in Figures 2 and 3. The difference in mechanical behavior was clearly observed among the samples. From Figure 2, it can be seen that the sample with high sucrose concentration (SC/MD = 7/3) exhibited a liquid-like behavior (G" > G') in the range of approximately 0.1 to 30 Hz, the so-called viscous region, in which the viscoelasticity increased more than an order of magnitude. In this region, the

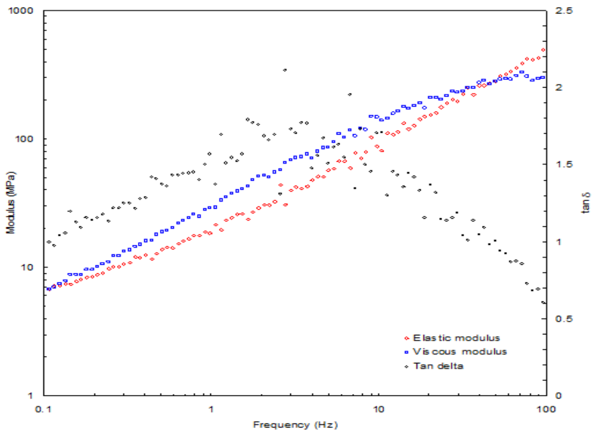

Figure 2. Representative dynamic moduli and tan δ as a function of frequency for the rubbery saccharide mixture with SC/MD of 7/3. Data were obtained at 25°C.

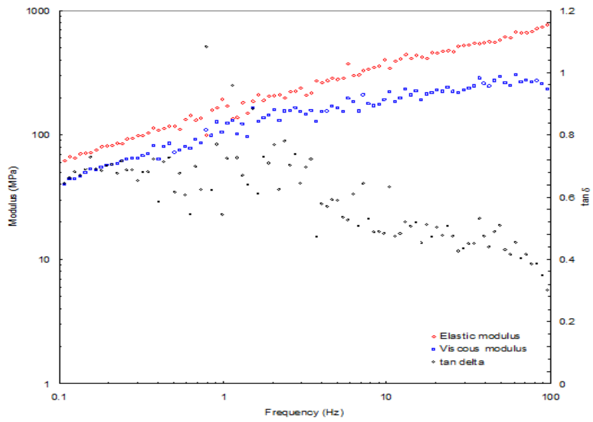

Figure 3. Representative dynamic moduli and tan δ as a function of frequency for the rubbery saccharide mixture with SC/MD of 3/7. Data were obtained at 25°C.

dominance of viscous component arises as a result of energy that is generated by molecular motions dissipates as heat during sinusoidal deformation (Kasapis and Sablani, 2005). At higher frequencies, a solid-like behavior was observed (G' > G"). The sample with SC/MD of 5/5 showed comparable magnitudes of G' and G" in a frequency range of 0.1 – 2 Hz before G' began to take over afterwards (Data not shown). In contrast to sucrose-rich mixture, the sample with high maltodextrin concentration (SC/MD of 3/7) exhibited a solid-like behavior over the entire range of applied frequency (Figure 3).

It was also found that the rigidity of samples increased with maltodextrin concentration. An amorphous matrix of saccharide system is basically formed up with two chemical bonds: hydrogen bonds and glycosidic linkages. The later was reported in prior study that it could restrict the movement of pyranose rings stronger than the other (Imamura *et al.*, 2006). Given the same number of pyranose rings, maltodextrin would possess higher density of glycosidic linkages than sucrose. This should, to a certain level, explain the increase in the rigidity with high maltodextrin concentration.

To further investigate the mechanical relaxation process, tan δ values were plotted against angular frequency (ω) as shown in Figure 4. In general, mechanical relaxation process extends over several decades of frequency – could be much broader than the range in this study. Nevertheless, it appeared that the majority of mechanical relaxation process of rubbery saccharide samples was captured in the frequency range studied. The sample with high sucrose concentration (SC/MD = 7/3) exhibited the strongest relaxation process with the maximum tan δ, or the loss peak height, of approximately 1.7 – 2.2. The value of tan δ greater than unity indicates the dominance of G" over G'. As such, the viscoelastic behavior in this region would be mainly governed by the motions of small molecules – sucrose, and partly by the configurational vibrations of segments (Ngai and Plazek, 1995; Kasapis and Sablani, 2005) of maltodextrin molecules. When the concentrations of sucrose and maltodextrin were equal (SC/MD = 5/5), the relaxation process was no longer dominated by the viscous component. There was more contribution from elastic component to viscoelastic behavior, and both components were equally significant. The increasing significance of elastic component might arise from the motions, which involve bending and stretching of glycosidic linkages in maltodextrin molecules (Kasapis and Sablani, 2005). It appeared that the more contribution from stretching and bending of glycosidic linkages in maltodextrin molecules gave rise to an elastic-dominant characteristic of the relaxation process observed from the sample with high maltodextrin concentration (SC/MD = 3/7).

There are several different relaxation processes that could be observed in mechanical or dielectric measurements. The two most common processes reported in literature are α- and β-relaxation. The β-relaxation takes place at a higher frequency (or lower temperature). In the vicinity of glass transition, the strength of α-relaxation is usually much higher than that of β-relaxation (Shinyashiki *et al.*, 2008). The α-relaxation is highly sensitive to water; the process shifts to lower temperatures (or higher frequency) as moisture content increases. This is not the case for β-relaxation (Noel *et al.*, 2000; Shinyashiki *et al.*, 2008). It has also been reported that the temperature dependence of α-relaxation is of the same order as that for $T_{g',DSC}$ depression as a result of plasticization by water (Noel *et al.*, 2000).

In some literature, the term $T_{g,DSC}$ may be designated for calorimetric glass transition temperature as to differentiate it from that inferred

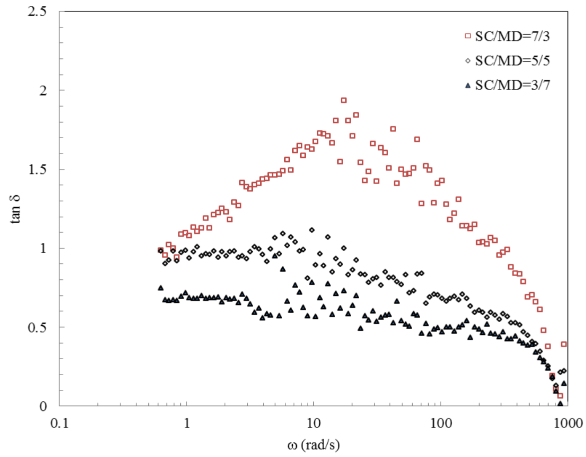

Figure 4. Frequency dependence of tan δ for rubbery saccharide systems. Data are means of two replicates obtained at 25°C.

from other techniques, for example, the dielectric or mechanical glass transition temperature ($T_{g,\alpha}$). To obtain T_g which is comparable to $T_{g,DSC}$, the $T_{g,\alpha}$ is conventionally defined as the temperature at which the characteristic time of α-relaxation process ($\tau_{,\alpha}$) is 100 s which is equivalent to ω = 0.01 rad/s, given ω = 2πf. In this study, it seemed like the vibrational frequency of the relaxation process (at 25°C) was in a range of approximately 1 – 20 rad/s depending on molecular elements in the mixture. Among all, the sample with SC/MD of 7/3 showed a relaxation peak at the highest frequency, while this peak for the sample with SC/MD of 3/7 was found at the lowest frequency range. Even though the entire relaxation process was not observable in our experiments, it could be speculated that if the measurements were carried out at temperatures lower than 25°C, the vibrational frequency of relaxation process would eventually reach 0.01 rad/s, which is the $T_{g,\alpha}$, by definition. The expected $T_{g,\alpha}$ would be much lower than the T_g,DSC obtained in the first part of this study (Table 1). This is not surprising since the moisture contents were much different, approximately 10% in SAOS compared to less than 4% in DSC measurements. A moisture difference of just 1% could lead to a substantial T_g depression, for instance T_g,DSC of the sample with SC/MD of 7/3 dropped from approximately 87°C to 59°C as the moisture content increased from around 0.3 to 2.8% (Table 1). A dramatic T_g,DSC reduction of dry amorphous D-Glucose for 56°C when moisture content increased to 10% (w/w) has been reported in literature (Noel *et al*., 2000).

Conclusions

Moisture content and the types of glass-forming molecule significantly affected the glass transition characteristics and mechanical behavior of amorphous saccharide mixture. Water strongly plasticized sucrose-maltodextrin mixture in that the increase in moisture content from 0.32 to 3.39% (wb) could suppress the T_g of the mixture from approximately 108°C to 64°C by average. Water also affected the glass transition dynamic of the mixture. Within the range of this study, the plasticization effect of water on sucrose and maltodextrin was comparable. Sucrose—small saccharide—contributed to a viscous-dominant or liquid-like behavior while large saccharide like maltodextrin lead to an elastic-dominant or solid-like behavior and the increasing rigidity of the mixture.

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