Impact of Caramelization on the Glass Transition Temperature of Several Caramelized Sugars. Part I: Chemical Analyses

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This study aims to investigate the relationship between caramelization of several sugars including fructose, glucose, and sucrose and their glass transition temperature (T_g). Differential scanning calorimetry (DSC) was used for creating caramelized sugar samples as well as determining their glass transition temperature, which was found to decrease first and then increase as the holding time at the highest temperature increased. The extent of caramelization was quantified by UV−vis absorbance measurement and high-performance liquid chromatography analysis. Results showed that the amount of small molecules from the degradation of sugar increased very fast at the beginning of heating, and this increase slowed down in the later stage of caramelization. On the other hand, there was a lag phase in the formation of large molecules from the degradation of sugar at the beginning of heating, followed by a fast increase in the later stage of caramelization. The obtained results clearly indicate the impact of melting condition on the T_g of sugars through formation of intermediates and end products of caramelization. Generally, when the heating condition is relatively mild, small molecules are formed first by decomposition of the sugar, which leads to a decrease of the overall T_g, and as the heating time becomes longer and/or the heating condition becomes more severe, polymerization takes over and more large molecules are formed, which results in an increase of the overall T_g. Mathematical modeling of the relationship will be presented as part II of the study in a separate paper.

INTRODUCTION

A glass is an amorphous solid characterized by having only short-range molecular arrangement but lacking long-range molecular packing (*1*). Many food-processing techniques could introduce amorphous structure, including spray drying (*2*), rapid cooling (*3*), freeze drying (*4*), and extrusion (*5*). Thus, many processed food materials exist in the amorphous or partially amorphous state, such as instant coffee and breakfast cereal. Glass transition is named for the phenomena observed when a glass is changed to a supercooled melt during heating or the reverse transformation during cooling (*6*). The glass transition temperature (T_g) refers to the temperature range where this transition occurs or a designated temperature within this range. The T_g value is usually considered as a reference temperature. Glassy food products are expected to be rigid and stable, although enthalpy relaxation below the glass transition temper-

ature could still play a significant role in food stability (*6*). On the other hand, food products containing a rubbery or liquid phase are expected to be soft and prone to physical, chemical, and biological changes, and the difference between the T_g and the storage temperature is assumed to control the rate of these changes (*5, 7*). Therefore, the study of T_g can help to predict and control the stability of food products during processing and storage. Although T_g can be measured by different methods including differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), and nuclear magnetic resonance (NMR), DSC has been the most commonly used method for the measurement.

Sugar is a commonly used ingredient in the food industry for its sweetness, texture, and preservative properties if used in high concentrations. Under high temperature treatments, the degradation of sugar happens by a complex series of reactions known as caramelization (*8*). Caramelization involves degradation of the sugar molecules and polymerization of the reaction intermediates and reactants. The reaction products normally give a special aroma and color, known as the caramel flavor and color. Because of the change of chemical composition by

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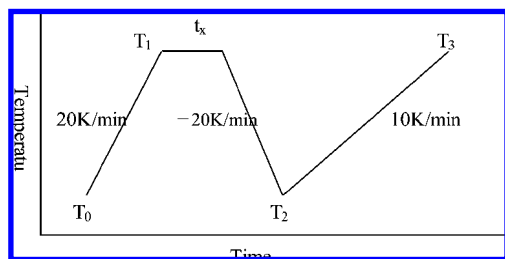   † National University of Singapore.
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Figure 1. Thermal history of sugars experienced in DSC.

Table 1. Final Heating Temperature (T_1) and Holding Time (t_x) for Creating Caramelized Sugar Samples[a]

type of sugar	final heating temperature T_1 (°C)	holding time t_x (min)
fructose	160	0, 2, 4, 7, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 90
	170	0, 2, 4, 8, 10, 12, 15, 20, 25, 30, 35, 40, 45, 50, 60, 70
glucose	180	0, 2, 4, 6, 8, 10, 15, 20, 30, 40, 50, 60, 70, 80, 90, 100, 110
	190	0, 2, 5, 6, 7, 10, 20, 30, 40, 50, 60, 70, 80, 90, 100
sucrose	205	0, 1, 1.25, 2.5, 3.75, 5, 6.25, 7.5, 10, 12.5, 15, 17.5, 20, 25, 30, 40

[a] Samples with minimal caramelization were yielded under t_x = 0 min and T_1 = 150, 170, and 200 °C for fructose, glucose, and sucrose, respectively. The corresponding T_g values were 12.0 °C for fructose, 39.3 °C for glucose, and 70.0 °C for sucrose.
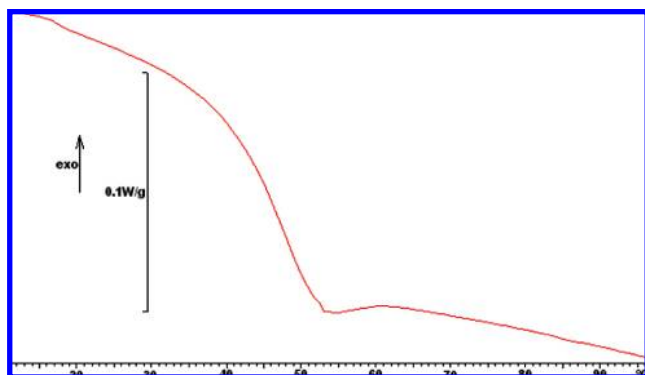

Figure 2. Typical DSC thermogram for T_g determination.

caramelization, the properties of the sugar caramel are different from those of the original sugar, which include T_g. Because the effect of a certain component in a mixture on T_g depends on its percentage in the mixture (9), for food products with a high sugar content, the T_g of sugar and sugar caramel plays a key role in the property of the food products. Therefore, thermal processing of a food product with a high sugar content may change the properties of the product itself considerably.

Many researchers have reported the T_g values of various types of amorphous sugar (10–12). However, the T_g values published by different authors vary considerably; for example, they range from 5 to 16 °C for fructose, from 35.4 to 38 °C for glucose, and from 68.5 to 78 °C for sucrose (6). These differences could be due to different thermal histories that the sugars have experienced, the presence of residual water, and the occurrence of caramelization reactions during T_g measurements by DSC (13). It has been found that decomposition of many types of sugar occurs near the vicinity of melting, which is an essential step to create amorphous sugar from sugar crystals in T_g

measurements using DSC (6). Generally, at a slow rate of heating, decomposition starts before melting, while at a fast rate of heating, it starts just after melting (14). Roos (13) studied the effect of caramelization on the calorimetric T_g of sucrose and proved that T_g depends strongly on the melting conditions of sucrose crystals. Until now, however, only the impact of caramelization on the T_g of sucrose was assessed qualitatively, where it was found that as the heating condition becomes more severe, the T_g of sucrose decreases with the appearance of small molecules and then increases with the appearance of polymerization products. However, there has been no report on other commonly used sugars such as glucose and fructose. Furthermore, there has been no report on quantitatively establishing the relationship between T_g of a caramelized sugar and its degradation and polymerization products, that is, mathematical modeling. A related issue is how to characterize the extent of caramelization of a sugar quickly and reliably.

The objective of this research was to study the changes in T_g of three types of amorphous sugar, that is, sucrose, glucose, and fructose, due to caramelization. The extents of caramelization will be assessed using UV–vis spectrometry and high-performance liquid chromatography (HPLC) analysis, and the impact of caramelization on the T_g of the sugars will be evaluated qualitatively in this paper as well as quantitatively via mathematical modeling in part II of this study in a separate paper.

MATERIALS AND METHODS

Materials. Three types of sugar including glucose (Aldrich, Steinheim, Germany), fructose (Sigma, St. Louis, MO), and sucrose (AnalaR, Poole, England) were used in this study. They were anhydrous and of HPLC grade. HPLC grade 5-(hydroxymethyl)furfural (HMF) of 99% purity was purchased from Aldrich (Steinheim, Germany).

Experimental Methods. DSC was used for the measurement of T_g values, and ultraviolet–visible (UV–vis) spectrometry and HPLC measurements were used for quantification of the extent of caramelization.

Caramelization Creation and DSC. A DSC (Mettler Toledo, DSC 821^e, Schwerzenbach, Switzerland) was used to create sugar caramels and to measure the T_g of samples. The sample sugar was first dried in a vacuum oven (Shellab, OR) at 60 °C and below 0.1 atm for 6 h. Then, approximately 2–12 mg of the dried sugar was placed into a 40 μL standard aluminum pan (Mettler Toledo) and hermetically sealed with an aluminum lid (Mettler Toledo). Nitrogen gas was used as both the purging gas and the protective gas with flow rates of 0.08 and 0.2 mL/min, respectively. Liquid nitrogen was used for cooling. Thermograms were analyzed by STAR^e Thermal Analysis System, version 8.01, which is a computational program for analysis of DSC results. The midpoint T_g was chosen as the glass transition temperature, and all of the T_g values in this paper refer to midpoint T_g unless otherwise stated. The thermal histories of the sugars are shown in **Figure 1**. First, a sample was heated from T_0 (25 °C) at 20 °C/min, then held at temperature T_1 for time t_x. Different extents of caramelization were created during this process. After that, it was cooled down to T_2 at −20 °C/min to create an amorphous state. Lastly, the sample was reheated to temperature T_3 at 10 °C/min, and T_g was determined from this step. T_2 was chosen to be about 60 °C below T_g, and T_3 was 40 °C above T_g.

After the thermal treatment and T_g measurement, the sample was dissolved in 1 mL of deionized water for further measurement. All of the samples were stored at −20 °C when not in use.

To study the relationship between caramelization and T_g, the melting condition, specifically the final heating temperature (T_1) and holding time (t_x) at the final heating temperature, were varied for different sugars, and the resultant T_g values were measured. **Table 1** lists the experimental conditions for creating various caramelized samples. Two different T_1 values were selected for fructose (160 and 170 °C) and
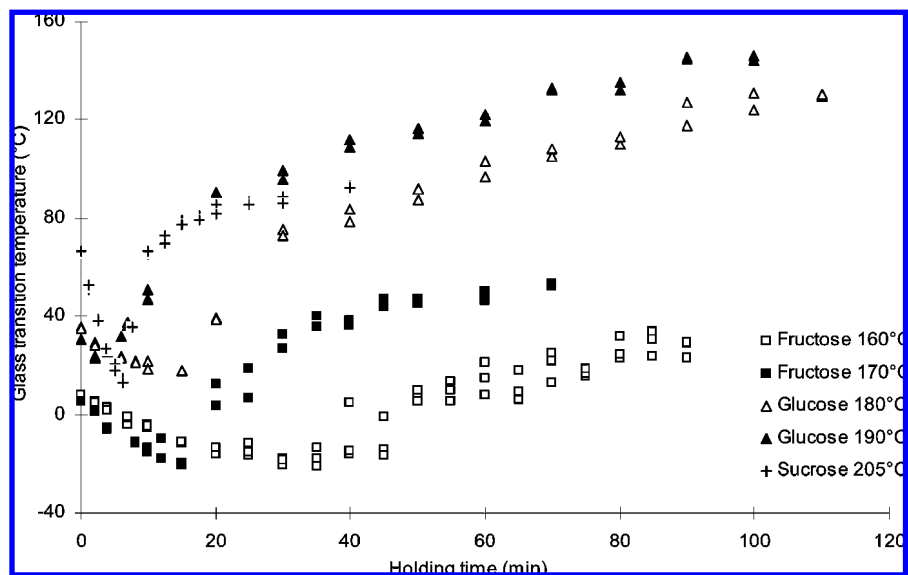
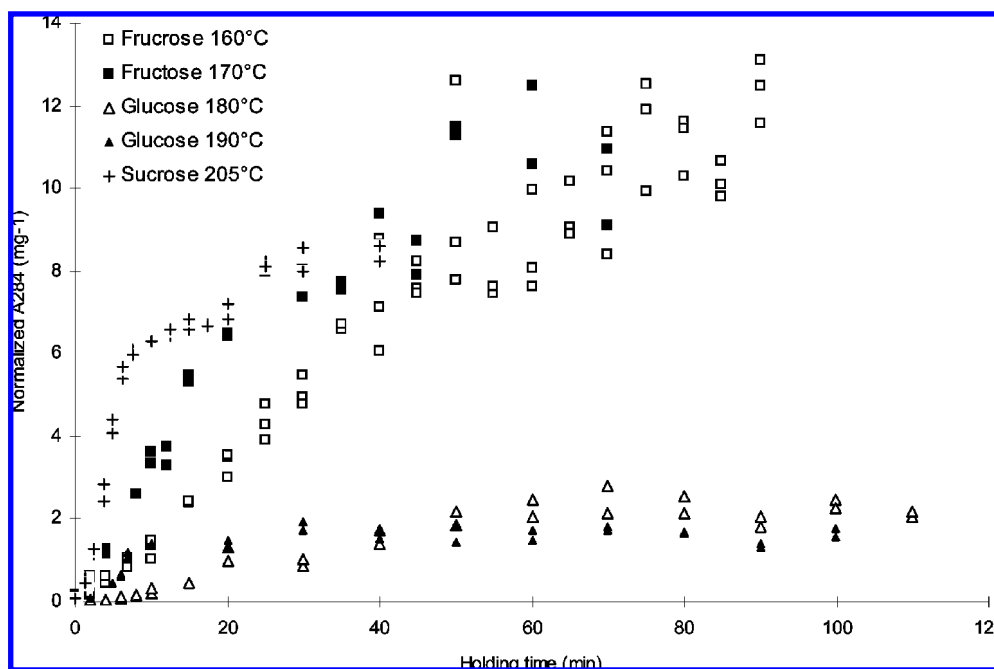**Figure 3.** Change of T_g with different holding time.

Figure 4. Change of normalized A_{284} with different holding time.

glucose (180 and 190 °C), whereas only one T_1 value was tested for sucrose (205 °C) since the influence of caramelization on the T_g of sucrose was already studied by Vanhal and Blond (*15*).

UV−Vis Spectrometry Analysis. After the DSC treatment and measurement, a sample was diluted to a suitable concentration so that the measured absorbance by a UV−vis spectrometer (Shimadzu UV-1700, Kyoto, Japan) was between 0.1 and 1 to ensure the accuracy of the measurements. Deionized water was used as a reference. Absorbances at 284 and 420 nm were recorded.

A calibration curve was created by making a series of HMF solutions and measuring their absorbances at 284 nm. The amount of HMF equivalent substances in a sample can be calculated based on its absorbance at the same wavelength.

HPLC Analysis. Sample solutions were analyzed by an HPLC system (Shimadzu, LC-10Avp) using Waters Sugar-PAK I Column with a size of 300 mm × 6.5 mm (Waters, Milford, MA), which is a cation exchange column packed with sulfonated styrene divinylbenzene resins in calcium form. A guard column of 1.5 cm in length with the same packing was used before the HPLC column. Deionized, bacteria-free

water was used as the mobile phase. Isocratic elution with a flow rate of 0.4 mL/min and a column temperature of 80 °C was used. The load volume was 10 μL. Sucrose, glucose, fructose, and HMF were quantified using the external standard method. Standards were prepared by dissolving the corresponding HPLC grade chemical in deionized water and serial dilution. Analysis of sucrose, glucose, and fructose employed a refractive index detector (RID) (Shimadzu), while a photodiode array (PDA) (Shimadzu) detector was used to analyze HMF at 284 nm.

RESULTS AND DISCUSSION

Glass Transition Temperature from Calorimetric Measurement. A typical DSC thermogram for T_g determination is shown in **Figure 2**. The T_g obtained varied over a wide range under different caramelization conditions (i.e., T_1 and t_x), as shown in **Figure 3**. Under each constant T_1 condition, as the holding time t_x increased, T_g decreased first to a lowest point,
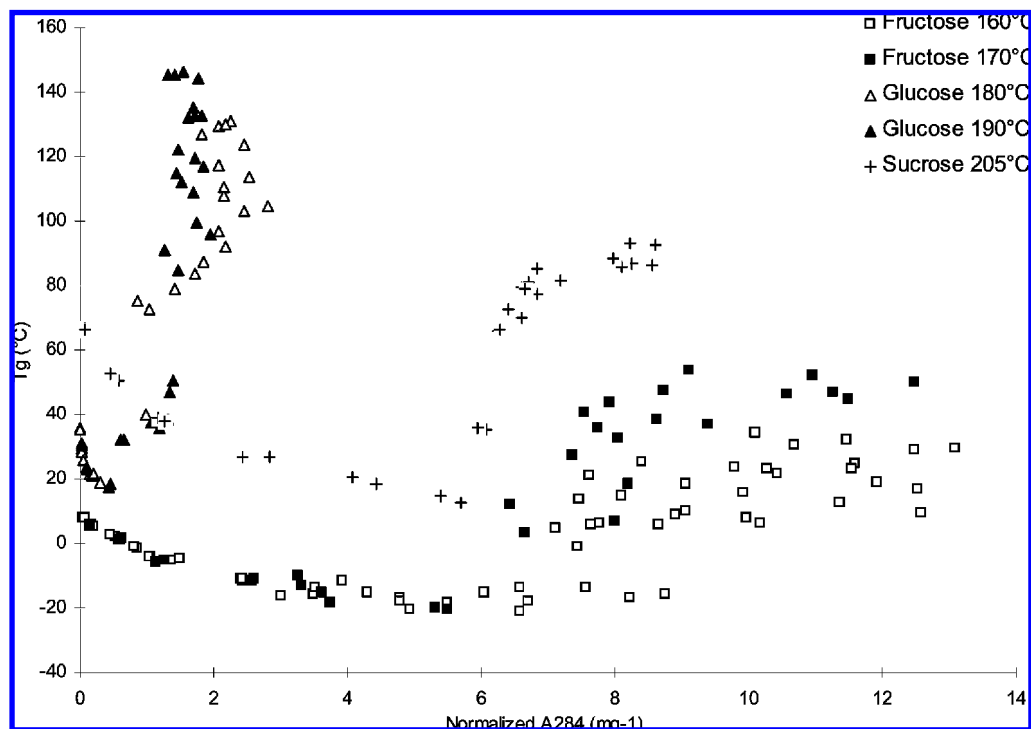
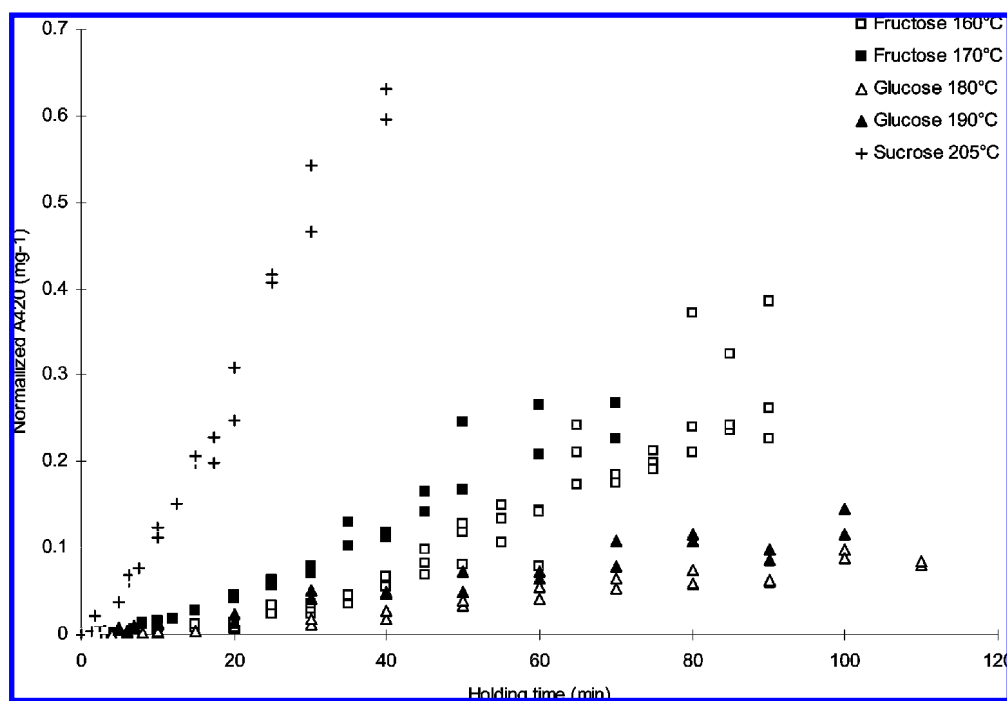**Figure 5.** Relationships between normalized A_{284} and T_g.

Figure 6. Change of normalized A_{420} with different holding time.

corresponding to a decomposition dominated phase (i.e., stage 1) and then climbed up toward a temperature higher than the initial T_g, corresponding to stage 2 where polymerization dominated.

The final heating temperature T_1 for sugars was chosen based on their respective melting peaks measured using DSC. The T_1 that was 20 °C above the melting point was studied for both fructose and glucose. In addition, T_1 values that were 30 and 10 °C above the melting points also studied for fructose and glucose, respectively. As caramelization of sucrose at 20 °C above its melting point proceeded extremely fast for sucrose,

T_1 that was 10 °C above its melting point was therefore chosen for it in this study.

From **Figure 3**, it appears that the longer the t_x is, the more inconsistent the T_g values from replicates were. The inconsistency of T_g was much more pronounced for fructose than either glucose or sucrose. The T_g values for all three types of sugars leveled off after the longest holding time, and insoluble products were also observed to have been formed at this stage.

As shown in **Figure 3**, glucose took the longest time among the three types of sugar to reach the final stage where T_g plateaued. On the other hand, sucrose took the shortest time to
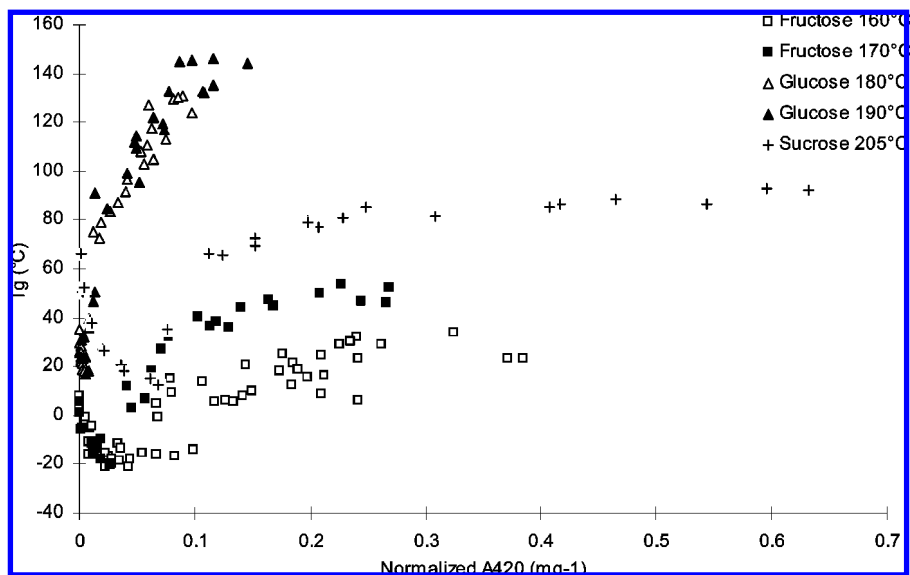
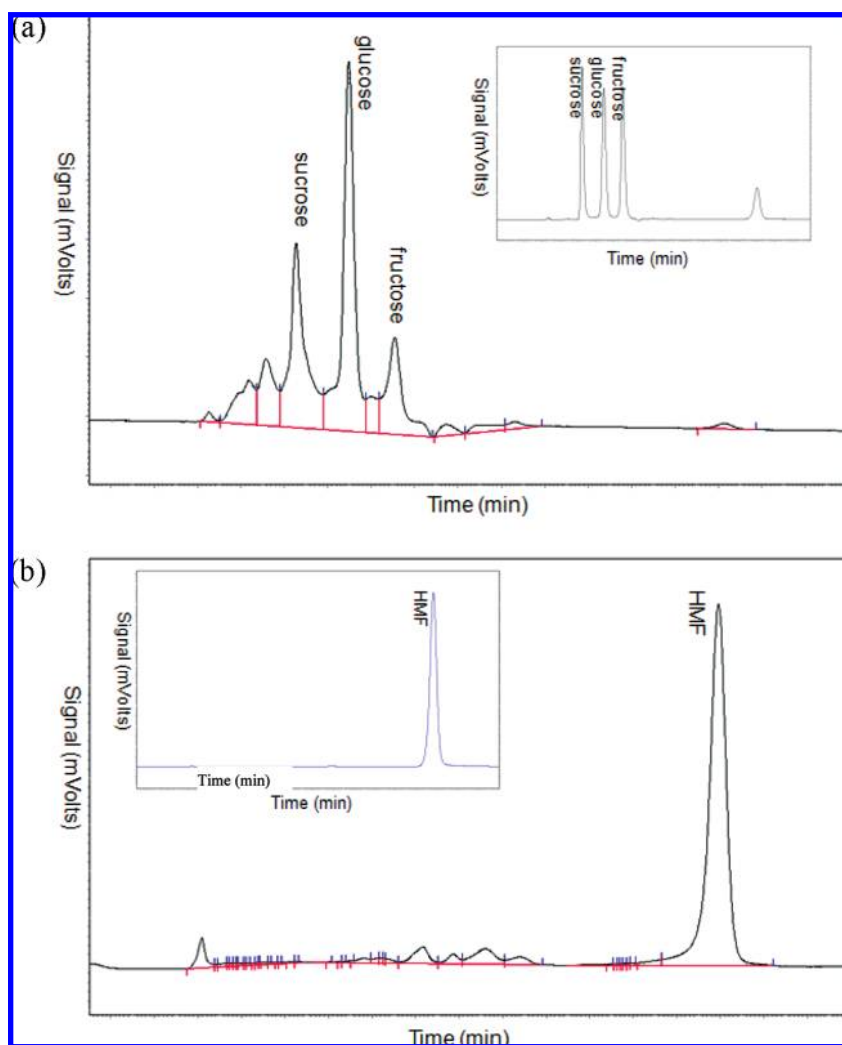**Figure 7.** Relationships between normalized A_{420} and T_g.

Figure 8. Examples of HPLC chromatograph. (**a**) Chromatograph of a caramelized sucrose sample RID with chromatograph of the standards RID in the insert. (**b**) Chromatograph of a caramelized sucrose sample PDA detector with chromatograph of the standard PDA detector in the insert.

reach this stage. This indicates that at the chosen temperatures, sucrose reacts the fastest, glucose reacts the slowest, and fructose is in between.

Because of the general rule that components that decrease the average molecular weight of the mixture will decrease the glass transition temperature (5), the decrease of T_g in the first
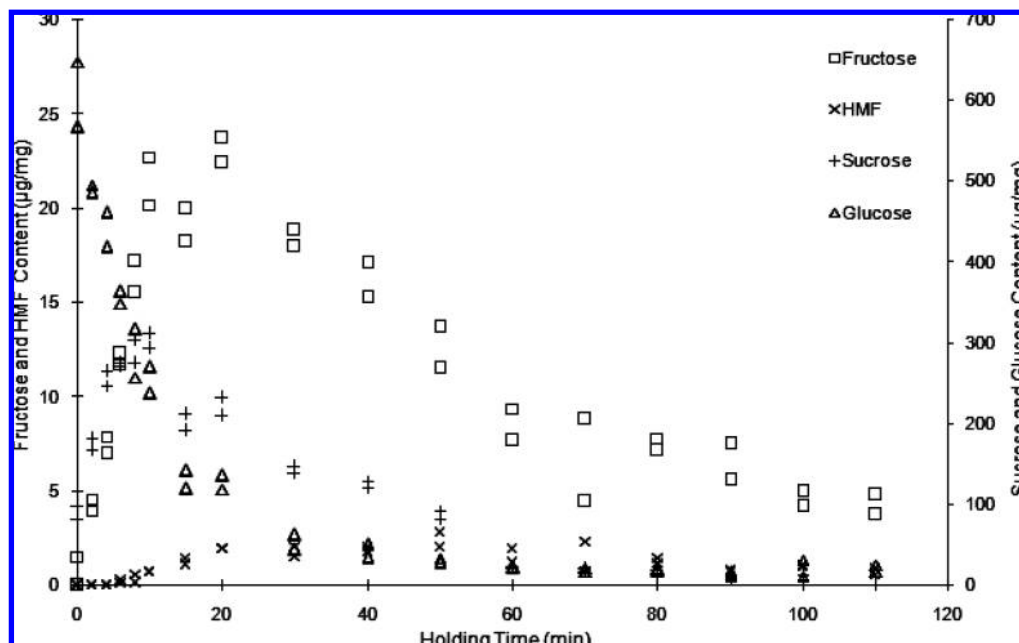
Figure 9. Change of reactant and intermediates with holding time during glucose caramelization.
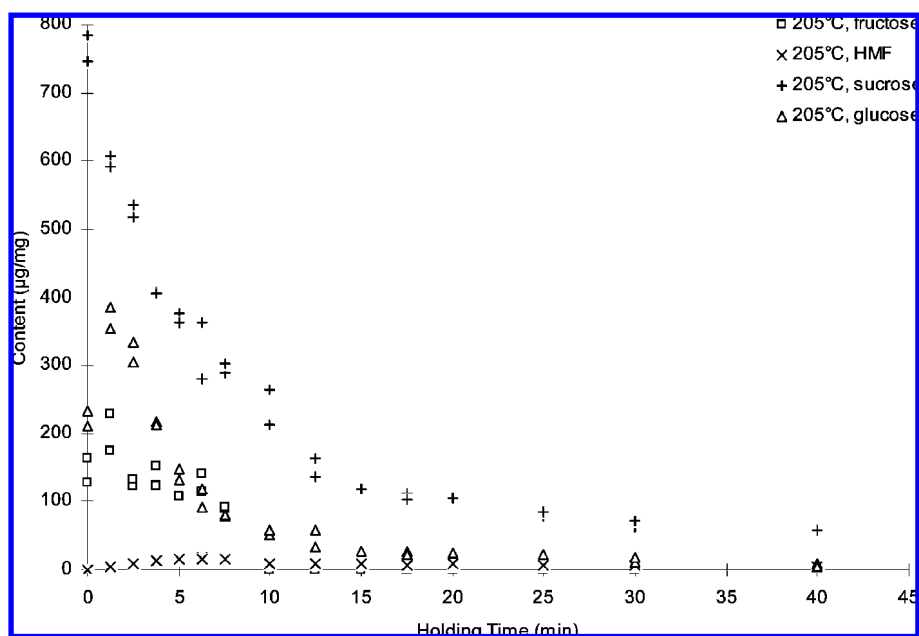

Figure 10. Change of reactant and intermediates with holding time during sucrose caramelization.

stage can be explained by the formation of a large amount of small intermediate compounds with their molecular weights lower than that of the original sugar during the first stage of caramelization. Besides small organic molecules formed during caramelization, another possible reason for the decreasing T_g is the formation of water. Sugar degradation during caramelization includes dehydration, which might result in an appreciable amount of water. Because water is a well-known powerful plasticizer, the formation and retaining of water within the DSC pan could result in a decrease of T_g of the mixture.

Vanhal and Blond (*15*) studied the impact of the melting condition of sucrose on its T_g. They studied the effect of the final heating temperature (T_1), holding time (t_x), and heating rate on T_g during melting. It was found that T_g decreased and then increased with increasing T_1 and that T_g decreased with decreasing heating rate or increasing t_x. The trend of

T_g's change with melting conditions was explained by the extent of caramelization, which is consistent with ours. However, it is worth pointing out that the experimental conditions on various t_x values and heating rates in ref *15* made the caramelization all within stage 1; therefore, only a decrease of T_g with caramelization was found under those conditions. In our study, varying the heating rate was not investigated, but the holding time (t_x) was dramatically extended to induce stage 2 of caramelization. Thus, we also observed that T_g increased following an initial decrease as t_x increased.

During caramelization, more polymerization occurs as the reactions continue, and polymerization will become dominant at a time that is reflected by the turn of T_g from decreasing to increasing. The polymerization reactions produce larger molecules with molecular weights higher than that of the original sugar; therefore, the T_g of the mixture increases.
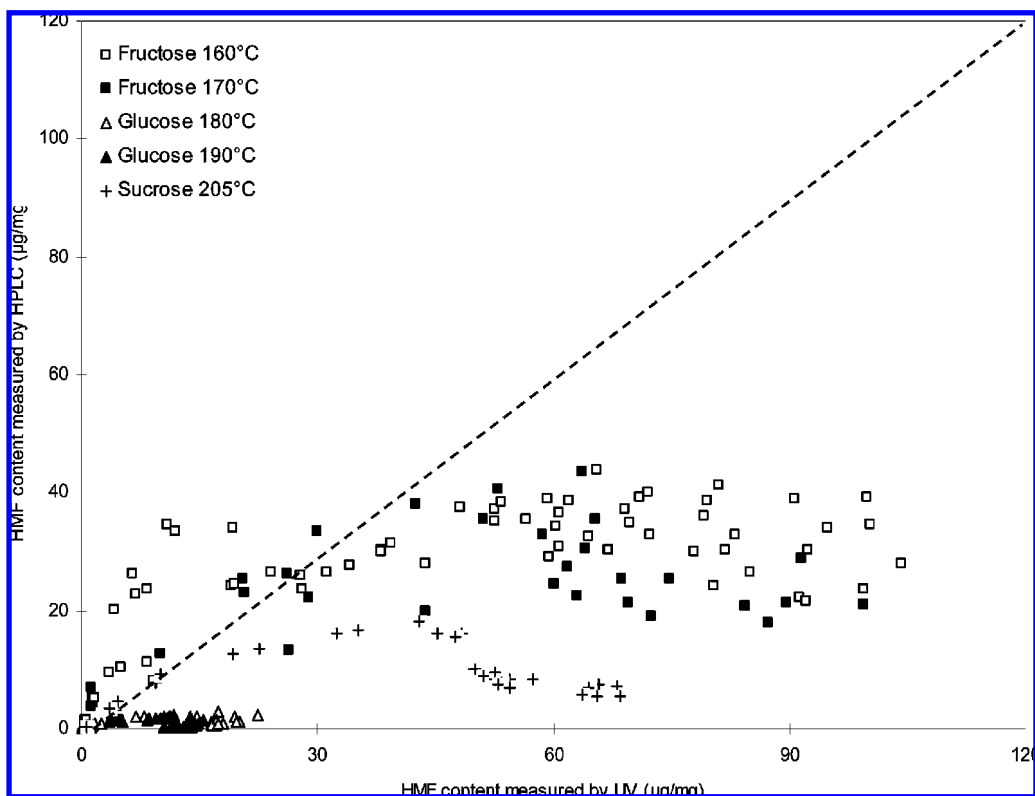
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Figure 11. Comparison of HMF content measured by UV absorbance and HPLC.
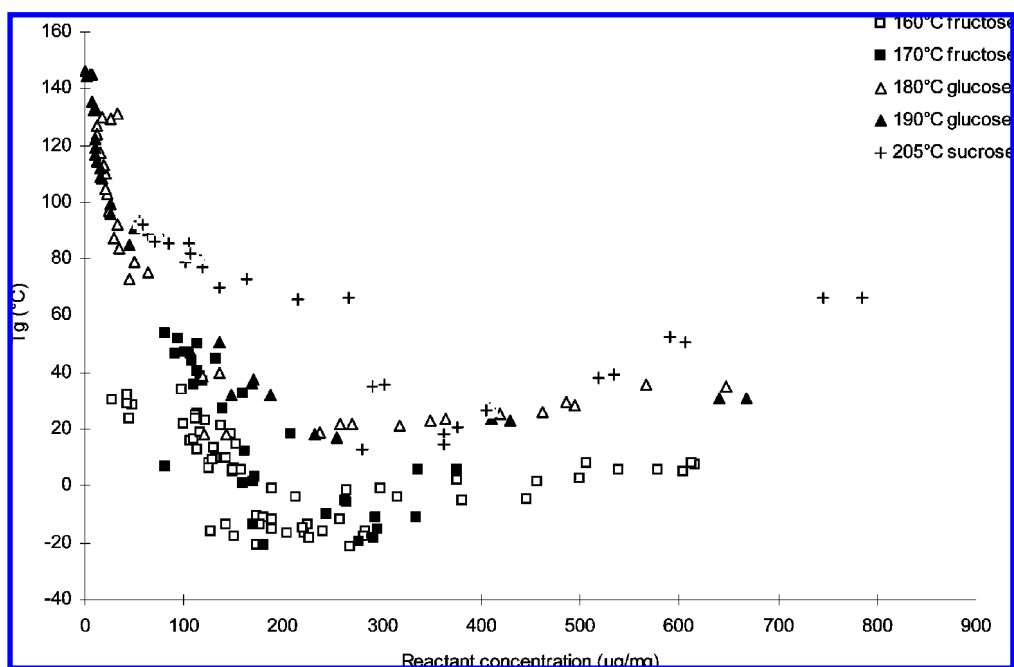

Figure 12. Change of T_g with reactants in sugar caramelization.

Eventually, when the holding time is long enough, T_g starts to level off. It was also observed that insoluble products started to form as the holding time increased. One possible reason for the leveling off of T_g is the limit of polymerization due to the shortage of intermediates needed.

The inconsistency in the replicates after a long holding time was due to the extensive caramelization reactions caused by prolonged heating. Large variation could be introduced especially when condensation reactions dominated, due to the large number of possibilities that the molecules could

react with each other and that many different combinations of product mixtures could be formed. In addition, because of the large amount of intermediates and end products formed in the reactions, the nonmiscibility of the compounds formed could also lead to the inconsistent T_g values. The more obvious inconsistent results of fructose caramelization were because of the faster and more extensive reaction of fructose than that of glucose because fructose can form 2,3-endiol in addition to 1,2-endiol, which can be formed by both fructose and glucose due to its ketose structure (*8*). In the case of

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sucrose, although many researchers found that the first step of sucrose caramelization is the splitting of the glycosidic bond to produce glucose and fructose carbocation, which could be converted to fructose (*16, 17*), the amount of fructose produced might not be very high since fructose carbocation is very reactive and many other parallel reactions involving fructose carbocation could occur that would limit the amount of fructose carbocation left for conversion to fructose. Therefore, the T_g values of caramelized sucrose were more consistent as compared to that of caramelized fructose.

The faster reaction of fructose than glucose is because the final heating temperatures chosen for fructose were well above its initial degradation temperature (147.1 °C), whereas the lower one of the two final heating temperatures used for glucose was around its initial degradation temperature (176.5 and 183.5 °C) (*14*). In the case of sucrose, the T_1 value used (205 °C) was also above its initial degradation temperature (200.7 °C); therefore, the products of initial degradation of sucrose, namely, fructose carbocation and glucose, would be subjected to high temperature used for sucrose caramelization. Because this temperature was much higher than the temperatures used in the caramelization of fructose and glucose alone, further degradation of fructose carbocation and glucose would be much faster. Therefore, it is possible that the further degradation of fructose carbocation and glucose produced by sucrose degradation leads to the faster reaction of sucrose.

Photospectrometric Measurement. HMF is a major stable intermediate at the beginning of caramelization/Maillard reactions, and its amount has been used to assess the extent of caramelization/Maillard reactions (*18, 19*). Absorbance at 284 nm was measured since HMF has its absorbance maximum at this wavelength, as shown by PDA chromatograph. Thus, measurement of A_{284} could serve as a fast and efficient way to examine the extent of caramelization. Absorbance at 420 nm has been used by researchers as a fast and reasonably accurate way to determine the yellowish brown color formed during caramelization and Maillard reactions (*18–21*). Because the major substance from caramelization absorbing at 284 nm (i.e., HMF) is a small molecule, in our study, A_{284} was used as an indicator of the amount of all small molecules that have plasticizing effects on T_g, rather than to quantify individual compounds produced during caramelization. On the other hand, absorbance at 420 nm is mainly caused by the high molecular weight molecules formed during caramelization, and it was used as an indicator of the amount of large molecules in the product mixture. The relationship between UV absorbance and T_g was investigated to evaluate the effect of high and low molecular weight compounds presented in the caramelized sugar on the overall T_g of the mixture.

Relationship between Absorbances and T_g. For the sugars tested in this study, the absorbance at 284 nm increased as the holding time increased at the beginning, and the increasing rate of A_{284} became smaller as the holding time became longer (**Figure 4**). A longer holding time indicates a more severe thermal treatment, and more caramelization products should be produced. Thus, the increase of absorbance at 284 nm might be due to the formation of substances absorbing at 284 nm during caramelization. However, at the later stage of caramelization, polymerization took over decomposition to become dominant. Some of these absorbing substances might be used for the formation of larger molecules, which could slow down the increase rate of A_{284}. In addition, the

rate of formation of the absorbing substances could also be limited by the concentration of reactants. The inconsistency observed in the increase of A_{284} with regard to T_1 at longer t_x in **Figure 4** could be a result of extensive caramelization under severe heating. It was also shown in **Figure 4** that although the A_{284} values of fructose and sucrose samples were close to each other, those of glucose were much lower. This could be attributed to the structural difference in the carbonyl group of ketose and aldose, of which the enolization step occurs more easily for a ketose sugar (*22, 23*); thus, more intermediates and products absorbing at 284 nm can be formed. The reactive carbocation from sucrose degradation could cyclize to form anhydride, add hydroxyl ion to produce fructose, or undergo nonspecific degradation to a wide range of products including HMF (*16, 17*). The formation of HMF and possibly other intermediates could contribute to the higher absorbance at 284 nm of caramelized sucrose.

Figure 5 shows that for all types of sugar studied, T_g decreased with increasing A_{284} in the first stage until the lowest T_g and then increased with increasing A_{284} in the second stage. The decrease of T_g with increasing A_{284} in the first stage of caramelization was due to the formation of small molecules indicated by the increasing A_{284}. In the second stage, although small molecules were still being formed (continuously increasing A_{284}), the formation of high molecular weight molecules became more extensive. Thus, the T_g increasing effect of these large molecules could become dominant and lead to an overall increasing T_g.

A_{420} increased as t_x increased, as shown in **Figure 6**. This is consistent with the observation that the longer the sugar was heated, the more intense the yellowish brown color was, due to the formation of yellowish brown pigments during caramelization, especially in the second stage. Similarly to that for A_{284} (**Figure 4**), larger inconsistency for A_{420} due to the inconsistency of the extensive reactions was observed in the later stage. The increase of A_{420} with t_x (**Figure 6**) showed a lag phase at the beginning of caramelization, because the high molecular weight compounds took some time to form from the small molecules produced initially. After the short lag phase, the rate of formation of colored compounds became almost constant, indicated by the almost linear relationship between A_{420} and holding time.

Figure 7 shows the relationship between T_g and A_{420}. T_g appeared to decrease with increasing A_{420} at a decreasing rate until the lowest T_g, and after that, T_g increased with increasing A_{420} at a decreasing rate, due to the different intermediates and end products formed during the two stages of caramelization as stated earlier.

HPLC Analysis. Chromatographs of the standards and a typical caramelized sugar sample detected by RID and PDA, respectively, are shown in **Figure 8**. The retention times of sucrose, glucose, fructose, and HMF are 9.78, 11.99, 14.04, and 28.72 min, respectively. The chromatograph of the caramelized sucrose sample analyzed by RID showed quite a lot of interference due to the universal nature of RID, while HMF is the dominant compound responding to PDA detector.

Figure 9 shows changes in the contents of fructose, HMF, sucrose, and glucose during glucose caramelization at 180 °C, while **Figure 10** shows changes of these compounds during sucrose caramelization at 205 °C. Caramelization of glucose at 190 °C yielded similar trends to those at 180 °C with faster changes of all the compounds because reactions proceeded faster at higher temperatures. Caramelization of fructose at 160 and 170 °C also produced similar trends to

those of glucose except that the trends of fructose and glucose swapped because fructose was now the reactant while glucose was the intermediate in the reactions. Generally, for all types of sugar, the amount of sugar as a reactant decreased throughout the thermal process. The amount of sugar was less than its initial amount even when t_x was 0, because although there was no holding at the highest temperature, the sugar had experienced high temperature during the process of heating up and cooling down, and caramelization reactions took place during these processes. In **Figures 9** and **10**, the compounds besides the original sugar increased first and then decreased. This trend indicates that these compounds were intermediates of the reactions, which were produced in the earlier stage and used up for further reactions in the later stage.

The well-known intermediate HMF presented at its highest concentration in caramelized fructose (figure not shown), followed by caramelized sucrose (**Figure 10**), and at a much smaller concentration in caramelized glucose (**Figure 9**). This might be due to the differences in the reaction mechanisms in caramelization of the sugars as explained earlier. Comparing the HMF content in the caramelized sugars measured by HPLC with the content of HMF equivalent in the caramelized sugars measured by UV−vis absorbance, the results from UV−vis absorbance gave a much higher value most of the time, as shown in **Figure 11**. This indicates that besides HMF, other reaction intermediates or products also absorbed at 284 nm.

Fructose formation in the glucose caramelization (**Figure 9**) and glucose formation in the fructose caramelization were due to the small amount of isomerization of the sugars (*25, 24*), while formation of fructose and glucose from sucrose (**Figure 10**) was because of the splitting of glycosidic bond of sucrose, followed by the addition of hydroxyl ion to fructose carbocation, which gave the individual monosaccharide (*16, 17*). For changes of the fructose content in sucrose degradation, Richards (*16*) stated that fructose was always produced in a lesser amount than glucose because not all of the fructose carbocation can be converted to fructose. In addition, fructose itself was subjected to faster further thermal degradation, as compared to glucose.

During the fructose and glucose caramelization, the sucrose content also increased first and then decreased, and the sucrose content could be as high as 30% of the whole sample (w/w) (**Figure 9**). The increase of sucrose content might be due to the isomerization between fructose and glucose followed by glycosidic linking, while the decrease might be caused by utilization of sucrose by thermal degradation. However, there has been no report in the literature on the formation of such a large proportion of sucrose during caramelization of fructose and glucose. Therefore, another possible reason is that the sucrose peak actually contained a group of reaction intermediates that could not be separated from sucrose by the column used. Further studies are required to verify this hypothesis.

T_g was also evaluated against the reactants during the caramelization of sugars (**Figure 12**). Generally, T_g decreased first and then increased with decreasing reactant content, which could be explained by the two stages of caramelization reactions.

In conclusion, DSC was used to create amorphous sugar caramel mixtures as well as to measure the T_g values of the mixtures. The resulting mixtures were evaluated by UV−vis measurement and HPLC analysis. It was found that in the first stage of caramelization, as holding time was increased, the formation of small molecules (indicated by A_{284}) dominated, which lead to the decrease of T_g values. On the other hand, when caramelization progressed into the second stage, as holding time was increased, the formation of large molecules (indicated by A_{420}) dominated, which lead to the increase of T_g values. However, relationships between T_g and chemical concentrations of the reactants and several measured major intermediates varied considerably and became inconsistent, particularly in the second stage of caramelization.

It becomes clear that the glass transition temperature of caramelized sugar changes with the extent of caramelization. To be able predict the glass transition temperature of caramelized sugar using simple measurements, relationships between the above-measured properties of caramelized sugar and their corresponding glass transition temperature were studied, and two sets of mathematical models were developed for T_g prediction. Details of the model development and the quality of the models will be reported in part II of this study.

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