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Discontinuous and heterogeneous glass transition behavior of carbohydrate polymer–plasticizer systems

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ABSTRACT

In order to understand the glass transition properties of carbohydrate polymer–plasticizer systems, glass transition temperatures of dextrin–glucose and dextrin–maltose systems were investigated systematically using differential scanning calorimetry. The onset (T_g^{on}) and offset (T_g^{off}) of the glass transition decreased with increasing plasticizer (glucose or maltose) content, and showed an abrupt depression at certain plasticizer content. The abrupt depression of T_g^{off} occurred at higher plasticizer content than that of T_g^{on}. The glass transition was much broader for intermediate plasticizer content. From the enthalpy relaxation behavior of samples aged at various temperatures, it was found that two different glass transitions occurred contentiously in the broad glass transition. These results suggested that carbohydrate polymer–plasticizer systems can be classified into three regions: the entrapment of the plasticizer by the polymer, the formations of the polymer–plasticizer and plasticizer-rich domains, and the embedment of polymer into the plasticizer.

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1. Introduction

Carbohydrate materials in biological, pharmaceutical and food products are usually in an amorphous state, and thus show glass transitions at a glass transition temperature (T_g). At temperatures below T_g, amorphous materials adopt a rigid glassy state, and they have limited macroscopic molecular mobility. In contrast, glassy materials adopt a soft rubbery state at temperatures higher than T_g, and amorphous materials have higher molecular mobility. Since various physico-chemical properties change drastically at T_g, it is important to understand the T_g of carbohydrate materials (Le Meste, Champion, Roudaut, Blond, & Simatos, 2002; Levine & Slade, 1988; Roos, 1995).

Water is known to play a significant role as a plasticizer in amorphous carbohydrate materials. This means that the T_g of amorphous carbohydrate materials decreases drastically with increasing water content, and thus the transition from a glassy state to a rubbery state occurs even at constant temperature. Consequently, there are many studies on the T_g change of not only carbohydrate–water systems (Avaltroni, Bouquerand, & Normand, 2004; Bizot, Le Bail, Leroux, Davy, Roger, & Buleon, 1997; Claude & Ubbink, 2006; Icoz, Moraru, & Kokini, 2005; Kawai, Fukami, Thanatuksorn, Viriyarattanasak, & Kajiwara, 2011; Orford, Parker, Ring, & Smith, 1989; Roos, 1993; Roozen, Hemminga, & Walstra, 1991), but also carbohydrate-enriched food–water systems (Bai, Rahman, Perera, Smith, & Melton, 2001; Baroni, Sereno, & Hubinger, 2002; Goula, Karapantsios, Achilias, & Adamopoulos, 2008; Moraga, Martínez-Navarrete, & Chiralt, 2004; Moraga, Martínez-Navarrete, & Chiralt, 2006; Silva, Sobral, & Kieckbusch, 2006; Sobral, Telis, Habitante, & Sereno, 2001; Syamaladevi, Sablani, Tang, Powers, & Swanson, 2009). The dependence of T_g on water content has been described by the Gordon–Taylor (GT) equation (Eq. (1)) and/or the Couchman–Karasz (CK) equation (Eq. (2)),

$$T_g = \frac{W_1 T_{g1} + k(1 - W_1)T_{g2}}{W_1 + k(1 - W_1)} \quad (1)$$

$$T_g = \frac{W_1 \Delta C_{p1} T_{g1} + (1 - W_1)\Delta C_{p2} T_{g2}}{W_1 \Delta C_{p1} + (1 - W_1)\Delta C_{p2}} \quad (2)$$

where T_{g1} and T_{g2} are T_g of the amorphous material and water, respectively, W_1 is the weight or mole fraction of the amorphous material, k is a constant depending on the system, and ΔC_{p1} and ΔC_{p2} are heat capacity changes of the glass transition of the amorphous material and water, respectively. However, it is unclear whether these equations are applicable to all mixing ratios of the carbohydrate–water system because it is very difficult to demonstrate the T_g change systematically; mixtures containing high water content show crystallization of water during the cooling process. In addition, it was reported that starch–water (Benczédi, Tomka, & Escher, 1998) and gelatin–water (Rahman, Al-Saidi, Guizani, & Abdullah, 2010) systems tend to deviate from these equations at

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high water content. Consequently, the glass transition behavior of carbohydrate–water systems remains a fundamental problem.

Materials with low T_g, such as mono- and di-saccharides, are also known to act as plasticizers for materials with high T_g, such as oligo- and poly-saccharides. Since carbohydrates readily adopt a solid glassy state by usual cooling treatment, the T_g of carbohydrate mixtures can be measured over a wide composition range. However, there are relatively few systematic studies on the T_g of carbohydrate mixtures. There are previous reports on the T_g change of maltotriose–glucose, maltohexaose–glucose, and maltohexaose–galactose systems (Orford, Parker, & Ring, 1990), sucrose–dextran system (Shamblin, Taylor, & Zografi, 1998), glucose–maltotriose system (Seo et al., 2006), sucrose–raffinose system (Saleki-Gerhardt & Zografi, 1994), and various molecular weights of dextran mixtures (Icoz et al., 2005). Carbohydrate with a low T_g and synthetic polymer mixtures, such as sucrose–polyvinyl pyrrolidone (PVP) (Shamblin, Huang, & Zografi, 1996; Shamblin et al., 1998), sucrose–Ficoll (Shamblin et al., 1996), and sucrose–PVP, trehalose–PVP, and raffinose–PVP (Taylor & Zografi, 1998) systems were also studied. Most results showed that the T_g of the mixtures decreased with increasing plasticizer content, and that the T_g depression was "roughly" described by the GT (Eq. (1)), CK (Eq. (2)), and other related equations. It should be noted that some results showed obvious deviation from the equations, similar to a part of polymer–water systems (Benczédi et al., 1998; Rahman et al., 2010).

Differential scanning calorimetry (DSC) has often been used for T_g studies of amorphous carbohydrate materials. T_g can be determined as an onset point of the endothermic baseline shift. Although many previous studies focused only on the onset point, the offset point also provides important insights into glass transition properties. For example, it is known that the difference between the onset and offset points of a glass transition reflects the temperature dependence of molecular mobility around T_g (Hancock, Dalton, Pikal, & Shamblin, 1998; Moynihan, 1993), the distribution of molecular mobility (Sartor, Mayer, & Johari, 1994), and the miscibility of the amorphous material (Shamblin & Zografi, 1998).

Previous studies are not sufficient to understand the effect of plasticizers on the T_g of carbohydrate materials. Thus, this study employed dextrin, which is a typical carbohydrate polymer, and the plasticizing effect of glucose and maltose on the T_g of the mixtures was investigated by DSC. The mixtures readily adopt a glassy state, and an apparent glass transition is observed in the DSC thermogram. In addition, since they are composed of only glucose, the mixtures are expected to be in a homogeneous amorphous state. Consequently, dextrin–glucose and dextrin–maltose systems are suitable samples for the purpose of this study.

2. Materials and methods

2.1. Sample preparations

Dextrin (from corn, type 1, reducing sugar ≤5%), α-D-glucose (anhydrous, 96%), and D-(+)-maltose monohydrate (grade 1, ≥98%) were purchased from Sigma–Aldrich Co. A 10% (w/w) aqueous solution for each reagent was prepared by dissolving the reagent in distilled water in a beaker. The solutions were placed in a 50 ml glassy vial, and then 10 ml of dextrin–glucose and dextrin–maltose solutions adjusted to various weight fractions were prepared. The solution was placed in a freezer before freeze-drying. The frozen preparations were placed in a pre-cooled freeze-drier, and vacuumed at a pressure below 70 Pa with increasing temperature from −40 °C to 10 °C over a period of 2.5 days. Furthermore, the residual moisture of the freeze-dried samples was removed at room temperature for 18 h in a vacuum desiccator. The obtained samples were stored hermetically in the vial. Hereafter, the samples are described by the weight fraction of plasticizer: "dextrin:glucose = 0.9:0.1 mixture" and "dextrin:maltose = 0.9:0.1 mixture" as "G0.1" and "M0.1", respectively.

2.2. DSC measurements

Glass transition properties of the samples were investigated by DSC (DSC120; Seiko Instruments Inc., Tokyo, Japan). Alumina was used as a reference, and the temperature and heat flow were calibrated by indium and distilled water. The samples (4–12 mg) were placed in an aluminum pan and held at 105 °C for 18 h. Then, the anhydrous samples were hermetically sealed in the pan. In order to avoid crystallization of glucose, G0.6, G0.7, and G0.8 were dehydrated at approximately 60 °C for 18 h in a vacuum desiccator. G0.9 and G1.0 showed crystallization of glucose depending on the time after the sample preparation. G1.0 sample was used before the crystallization. The sample was warmed with stirring on a heater, and the viscous mixture was placed in the DSC pan. After the vacuum-dehydration at approximately 30 °C for 18 h, the sample was hermetically sealed in the pan. G0.9, on the other hand, caused crystallization of glucose before DSC measurement. The sample was placed in the DSC pan by the similar procedure to G1.0, and then DSC measurement was performed as follows; the crystallized glucose was melted in a first heat-scanning, and glass transition properties were investigated by a second heat-scanning after cooling to approximately 10 °C. DSC measurements were performed at 5 °C/min in the temperature range of 0 and 240 °C. The scanning was stopped at a certain temperature depending on T_g of the samples in order to prevent crystallization and/or thermal degradation during the measurement, and glass transition properties were investigated by a second heat-scanning after cooling to approximately 10 °C. The measurements were duplicated, and the onset ($T_g{}^{on}$) and offset points ($T_g{}^{off}$) of the glass transition were averaged.

3. Results

3.1. Glass transition behaviors of dextrin–glucose and dextrin–maltose systems

All samples except dextrin (non-additive sample) showed an apparent endothermic baseline shift due to the glass transition as shown in the DSC thermogram, and thus $T_g{}^{on}$ and $T_g{}^{off}$ were determined reasonably well. Dextrin, on the other hand, showed a large endothermic peak at approximately 198 °C, presumably because the thermal degradation of dextrin occurred simultaneously with the glass transition. In fact, the endothermic temperature agreed with $T_g{}^{on}$, extrapolated to anhydrous dextrin through the $T_g{}^{on}$ change of the dextrin–water system (data not shown). Similar results were also reported in previous studies: $T_g{}^{on} = 180$ °C for 155 kDa dextrin (Avaltroni et al., 2004) and $T_g{}^{on} = 198$ °C for 93 kDa dextrin (Claude & Ubbink, 2006). $T_g{}^{on}$ of dextrin used in this study was determined to be 198 °C. $T_g{}^{off}$ of dextrin, on the other hand, could not be determined for the reasons mentioned above.

Typical DSC thermograms for the dextrin–glucose system are shown in Fig. 1. G0.1 showed a glass transition at a lower temperature than dextrin (198 °C) due to the plasticizing effect of glucose. G0.2 showed a glass transition at an even lower temperature. In addition, its glass transition temperature range was broader than that of G0.1. This broad glass transition suggests the existence of multiple glass transitions at that temperature. G0.3, G0.4, and G0.5 showed trends similar to G0.2. In the DSC thermogram of G0.6, the glass transition behavior changed from a broad glass transition to a distinctive glass transition. Such glass transition behavior was also confirmed in G0.7, G0.8, G0.9, and G1.0. This indicates that the glass

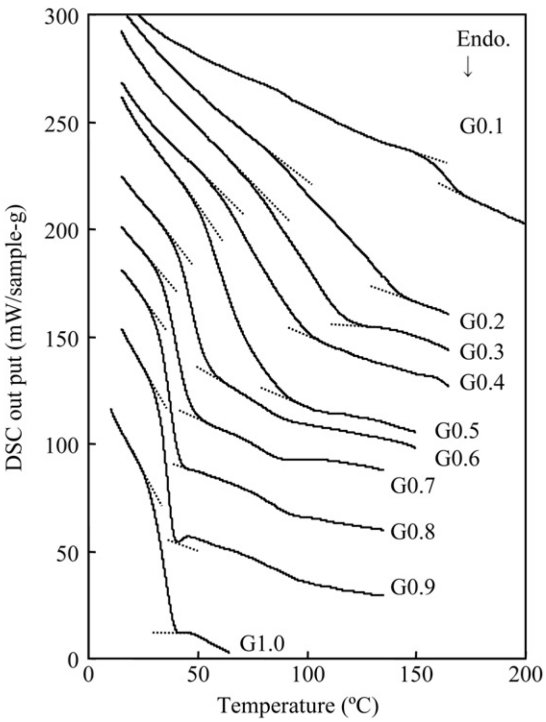

Fig. 1. Typical DSC thermograms for the dextrin–glucose system.

transition behavior of the dextrin–glucose system approaches that of glucose with increasing glucose content.

T_g^{on} and T_g^{off} were plotted against the weight fraction of glucose as shown in Fig. 2. The results confirmed that T_g^{on} decreased with increasing glucose content, but the T_g^{on} depression could not be described by a simple curve; T_g^{on} decreased discontinuously between G0.1 and G0.2. T_g^{off} also decreased with increasing glucose content, and showed an abrupt depression between G0.5 and G0.6. Samples between G0.2 and G0.5 showed a broader glass transition than the other samples. From these results, it was found that the glass transition behavior of the dextrin–glucose system can be classified into three regions (A, B, and C) as shown in Fig. 2.

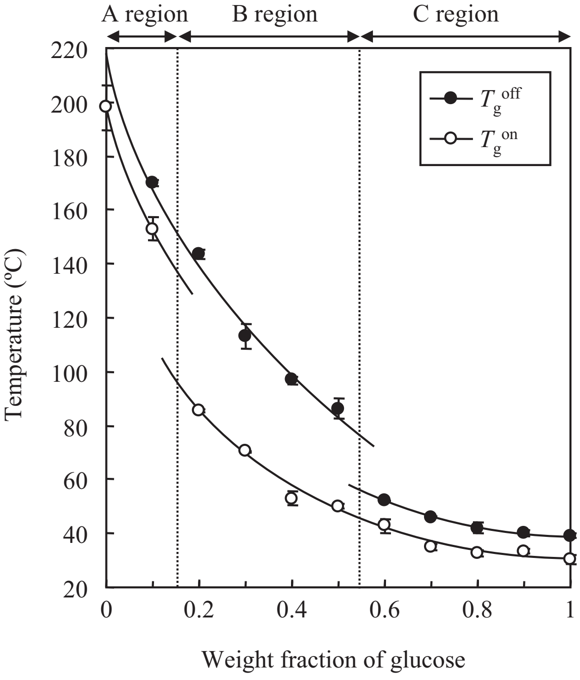

Fig. 2. T_g^{on}s and T_g^{off}s of the dextrin–glucose system.

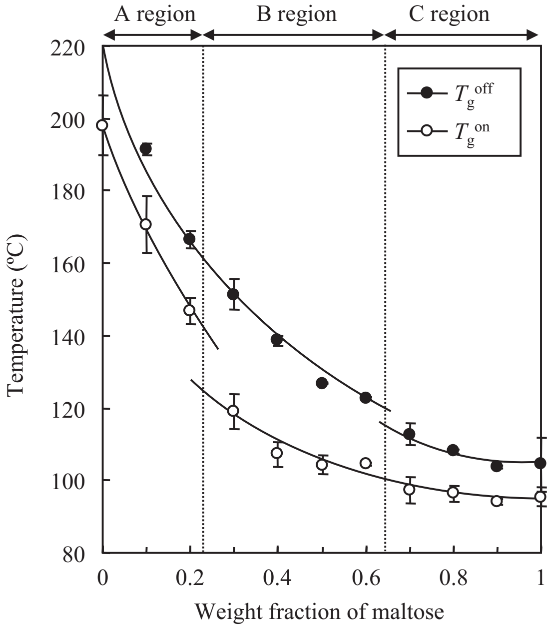

Fig. 3. T_g^{on}s and T_g^{off}s of the dextrin–maltose system.

T_g^{on} and T_g^{off} of the dextrin–maltose system were also determined, and the values were plotted against the weight fraction of maltose as shown in Fig. 3. T_g^{on} and T_g^{off} decreased with increasing maltose content, and showed abrupt depressions between M0.2 and M0.3 and between M0.6 and M0.7, respectively. These results suggested that the turning points of the T_g depression shifted to a higher plasticizer content than those of the dextrin–glucose system. In addition, the decrease in T_g^{on} and T_g^{off} was less than that of the dextrin–glucose system.

3.2. Enthalpy relaxation behavior of the dextrin–glucose mixtures

G0.2, G0.3, G0.4, and G0.5 showed a remarkably broad glass transition. In order to understand the origin of the broad glass transition, G0.4 was employed, and the enthalpy relaxation behavior was investigated by DSC. Enthalpy relaxation is a process in which the excess enthalpy of glass in a non-equilibrium thermodynamic state decreases spontaneously toward its equilibrium value. For example, enthalpy relaxation occurs during an isothermal holding treatment at temperatures below T_g (*i.e.*, aging). When the aged glass is heated to a temperature above T_g, an endothermic peak due to recovery of the relaxed enthalpy is observed simultaneously with the glass transition. Based on the relationship between the recovery of relaxed enthalpy and aging treatment, detection of an unclear glass transition, measurement of the molecular mobility of glassy materials, and confirmation of the miscibility of glassy mixtures were carried out (Borde, Bizot, Vigier, & Buléon, 2002; Bosma, Brinke, & Ellis, 1988; Chung, Lee, & Lim, 2002; Haque, Kawai, & Suzuki, 2006; Kawai, Hagiwara, Takai, & Suzuki, 2005; Sartor et al., 1994; Shamblin & Zografi, 1998).

DSC thermograms of G0.4 aged at various temperatures for approximately 16 h are shown in Fig. 4. G0.4 aged at a temperature between 30 °C and 60 °C showed two endothermic peaks in the glass transition. This indicates that two different glass transitions occurred contentiously in the broad glass transition (Bosma et al., 1988). When G0.4 was aged at 70 °C, a single endothermic peak was observed. This indicates that the aging temperature was lower than the high-temperature glass transition, but higher

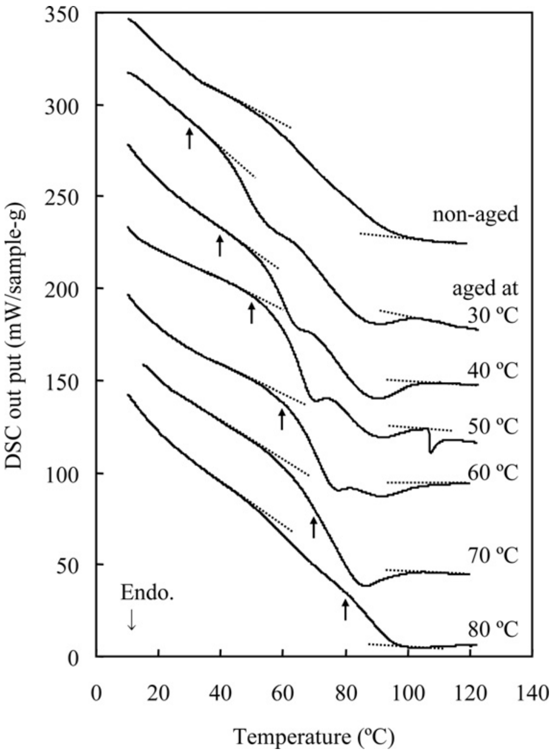

Fig. 4. Typical DSC thermograms for G0.4 before and after aging treatment for approximately 16 h. Upper arrows indicate the aging temperatures.

than the low-temperature glass transition; it should be noted that enthalpy relaxation occurs at temperatures below T_{g}. G0.4 aged at 80 °C showed no recovery of relaxed enthalpy because the aging temperature was higher than both the glass transitions.

4. Discussion

The dextrin–glucose and dextrin–maltose systems showed abrupt $T_{\mathrm{g}}^{\mathrm{on}}$ depressions between G0.1 and G0.2 and between M0.2 and M0.3, respectively. In previous systematic studies on the $T_{\mathrm{g}}^{\mathrm{on}}$ change of amorphous carbohydrate mixtures, the $T_{\mathrm{g}}^{\mathrm{on}}$ depression was roughly described as a simple curve. From this standpoint, the $T_{\mathrm{g}}^{\mathrm{on}}$ depression of the maltose–dextrin system may also be approximated as a simple curve. Although this is one possible interpretation based on previous studies, it is important to note the fact that the dextrin–glucose mixture showed a clearly discontinuous $T_{\mathrm{g}}^{\mathrm{on}}$ depression. This behavior is also reported in synthetic polymer–diluent systems (Ceccorulli, Pizzoli, & Scandola, 1987; Righetti, Ajroldi, & Pezzin, 1992). On the other hand, $T_{\mathrm{g}}^{\mathrm{off}}$ of dextrin–glucose and dextrin–maltose systems decreased abruptly between G0.5 and G0.6 and between M0.6 and M0.7, respectively, emphasizing the fact that there is still little information on the systematic $T_{\mathrm{g}}^{\mathrm{off}}$ change in amorphous systems.

The glass transition behaviors of dextrin–glucose and dextrin–maltose systems were classified into three regions as shown in Figs. 2 and 3. An amorphous structure model for the carbohydrate polymer–plasticizer system is suggested with a schematic drawing as shown in Fig. 5. At a low plasticizer content (A region), the polymer is plasticized by the plasticizer, and thus T_{g} of the system decreases with increasing plasticizer content. The plasticizer is entrapped by the polymer in the region, and thus the glass transitions of the mixture occur cooperatively. A part of the plasticizer "spills" from the entrapment of the polymer when the plasticizer content increases (B region). Then, polymer–plasticizer and plasticizer-rich domains are formed in the amorphous mixture. When the mixture is heated from a low temperature, the glass transition occurs in the plasticizer-rich domain and subsequently occurs in the polymer–plasticizer domain. Thus, the $T_{\mathrm{g}}^{\mathrm{on}}$ of the mixture decreases abruptly due to the plasticizer content

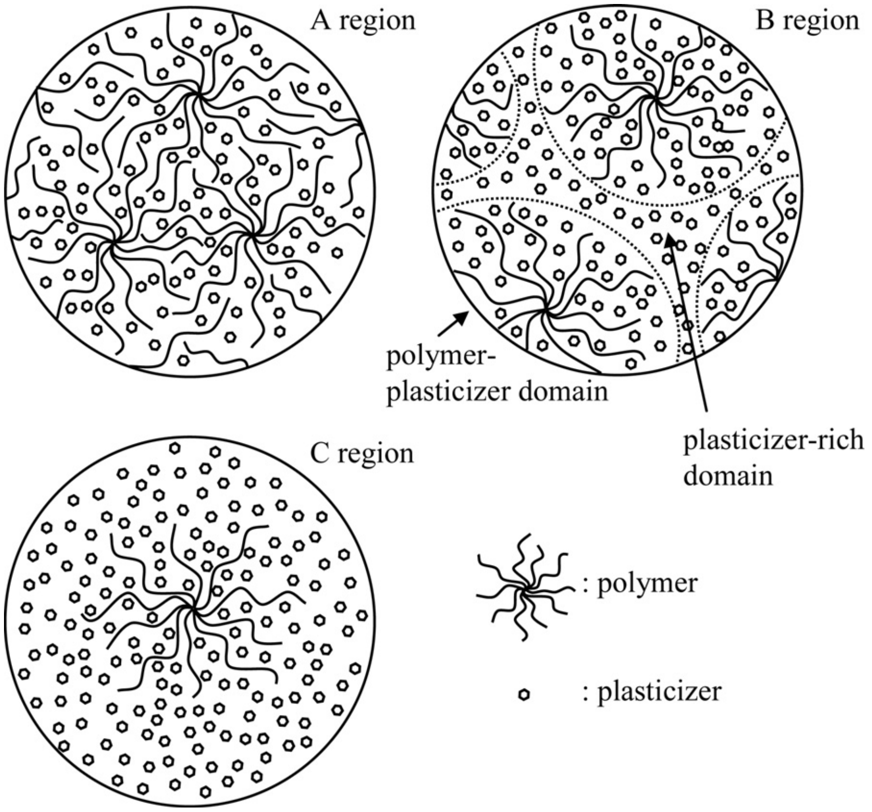

Fig. 5. Schematic drawing of the amorphous structure of carbohydrate polymer–plasticizer mixtures.

and the glass transition temperature range becomes broad. This phenomenon is not considered to be the "phase separation" of the mixture. If phase separation occurs in the mixture, individual T_gs of the polymer and plasticizer will be observed, as seen in the PVP–dextran mixture (Shamblin, et al., 1998). However, T_g^{on}s and T_g^{off}s of dextrin–glucose and dextrin–maltose systems gradually decreased with increasing plasticizer content. This indicates that the molecular mobility of the plasticizer-rich domain is affected by the polymer–plasticizer domain due to the domain–domain interaction. In a mixture with high plasticizer content (C region), the plasticizer-rich domain develops to the plasticizer's surroundings, and the polymer–plasticizer domain spreads out; the polymer is embedded in the glassy plasticizer, and the molecular mobility of the polymer is governed by the plasticizer. Consequently, T_g^{off} decreases abruptly, and a distinctive glass transition occurs, similar to the glass transition of a pure plasticizer. Results observed in protein–saccharide systems (Demmel, Doster, Petry, & Schulte, 1997) support the interpretation that the molecular mobility of a polymer is governed by the plasticizer.

The discontinuous and heterogeneous glass transition behaviors observed in the dextrin–maltose system were less than those of the dextrin–glucose system. This is because the plasticizing effect of maltose is less than that of glucose. In contrast, the greater plasticizer such as diluents may cause more remarkable features. For example, Mathew and Dufresne (2002) reported that the amylopectin–glycerol system (weight fraction of glycerol ≈0.33) showed two glass transitions at $-53.5\,^{\circ}\mathrm{C}$ and at $26.5\,^{\circ}\mathrm{C}$, and stated that these glass transitions were due to the glycerol-rich domain and amylopectin-rich domain, respectively. However, they found that the addition of sugar alcohols such as xylitol, sorbitol, and maltitol (having the same weight fraction as glycerol) did not cause the separation of the glass transition. Since the sugar alcohols are much larger molecules than glycerol, further addition of the sugar alcohols will be required for the formation of the plasticizer-rich domain.

Although this study showed that dextrin–glucose and dextrin–maltose systems have a single glass transition at low plasticizer content (A region), some previous studies suggested that sub-T_g due to an independent glass transition of plasticizer molecules entrapped by polymer is observed at a lower temperature than the major T_g caused by the polymer–plasticizer mixtures. This was seen in amylopectin–glycerol (Mathew & Dufresne, 2002), amylose–glycerol (Moates, Noel, Parker, & Ring, 2001), barley starch–glycerol–water (Forssell, Mikkilä, Moates, & Parker, 1997), and albumin–water (Kawai, Suzuki, & Oguni, 2005) systems. There are two possibilities as to why sub-T_g could not be observed in dextrin–glucose and dextrin–maltose systems. One is that DSC cannot detect such minor thermal response because of its limited accuracy. The other is that the appearance of low-temperature glass transition is a specific feature of solvents such as water and glycerol; it is noted that the solvent types of plasticizers are much smaller than the polymer, and that there is a large difference in their molecular mobility. In order to obtain further insights into the problem, adiabatic calorimeter and/or dielectric relaxation studies will be useful. This is one topic for future study.

5. Conclusion

Dextrin–glucose and dextrin–maltose systems showed a discontinuous and heterogeneous glass transition. T_g change of a carbohydrate polymer–plasticizer system cannot be described by a simple curve as predicted by GT (Eq. (1)) and/or CK (Eq. (2)). This is not always complicated for the prediction of T_g. The fact that T_g^{on} of the carbohydrate polymer–plasticizer system with high plasticizer content was strongly affected by the plasticizer-rich domain and/or the plasticizer's surroundings indicates that the T_g of a plasticizer is an important factor for T_g prediction. It should be noted that sugar-rich products (*e.g.*, dry fruits) usually show a low T_g value equivalent to that of monosaccharides such as glucose, fructose, and sucrose. These fundamental data will provide insights into better T_g prediction for amorphous carbohydrate products.

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