

Correlation Between Glass Transition Temperature and Starch Retrogradation in the Presence of Sugars and Maltodextrins¹

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ABSTRACT

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The stability of starch solutions containing sugars (glucose, fructose, maltose, and sucrose) and maltodextrin at concentrations of 6 and 9% was investigated. Differential scanning calorimetry was used to measure the retrogradation rate of gelatinized starch and to determine the specific glass transition temperature (T_g') of a maximally freeze-concentrated solution. Starch containing low molecular weight molecules had a lower T_g' than those containing high molecular weight molecules. Starch with glucose and fructose exhibited greater retrogradation than did starch with

maltose, sucrose, and maltodextrin after being stored at -20°C . The T_g' of starch samples containing sugars increased during storage. The temperature shift ranged from -0.7°C to $+4.4^\circ\text{C}$ for samples stored at 2°C , and -0.4°C to $+3.7^\circ\text{C}$ for samples stored at -20°C , after 21 days. The results indicated that the lower the ΔT value ($\Delta T = T_f - T_g'$) between the freezer temperature (T_f) and the T_g' of the sample, the greater the storage stability of foods.

Glass transition is the kinetic transition of polymers from a glassy state to a rubbery state; this occurs at a specific temperature, the glass transition temperature (T_g). This occurs in completely amorphous and partially crystalline polymers, including many food materials. The T_g is specific to each material and is affected by three major factors: molecular weight (MW), composition,

and plasticizer material (Fox and Flory 1950, Gordon and Taylor 1952). The T_g of a homologous glass-forming polymer increases with increasing number-average molecular weight (M_n) up to a plateau limit (Billmeyer 1984). The weight fraction of individual components determines the T_g of miscible polymers. A plasticizer is "a material incorporated in a polymer to increase the polymer's workability, flexibility, or extensibility" (Sears and Darby 1982). Water is an important plasticizer in polymers because of its low MW (LMW), which increases the free volume and decreases the local viscosity. It was not until the 1980s that food scientists recognized the importance of the T_g in food systems and used the T_g to predict product properties, quality, stability, and safety.

For frozen foods, the glass transition temperature (T_g') of a maximally freeze-concentrated polymer dispersion governs

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physical changes of food components under frozen conditions. Ice crystals grow during freezing, and thus the solute concentration increases as freezing progresses, eventually forming a maximally freeze-concentrated solution matrix. The unfrozen matrix reaches a constant solute concentration that is independent of the initial solute concentration at the T_g' . The matrix exists as a kinetically metastable, amorphous solid at temperatures below T_g' , but it is a viscous liquid at temperatures between T_g' and T_m' (the temperature when ice melts). It has been suggested that the stability of frozen foods is controlled by the temperature difference (ΔT) between the freezer temperature (T_f) and the T_g' of the specific solutes ($\Delta T = T_f - T_g'$) (Levine and Slade 1986). There is a positive correlation between T_g' and stability at a constant T_f . With the addition of LMW or HMW ingredients, the T_g' of the product changes, and the frozen storage stability changes accordingly. LMW carbohydrates, such as sugars, maltodextrins, and corn syrup, constitute a significant proportion in many fabricated foods. The T_g' of these small carbohydrates have been investigated by using differential scanning calorimetry (DSC) (Levine and Slade 1986, 1988; Roos and Karel 1991a,b; Roos 1993), and the resulting information has helped food scientists control storage stability and food product quality.

Starch retrogradation is a process in which gelatinized starch molecules reassociate to form a double-helix crystalline structure. Previous studies demonstrated that the addition of sugars enhanced starch gel retrogradation (Maxwell and Zobel 1978, Germani et al 1983, Chang and Liu 1991). Kohyama and Nishinari (1991), however, reported that sugars prevented retrogradation of sweetpotato starch paste and proposed that the sugar molecules interacted with starch molecular chains to stabilize the starch matrix and, thus, inhibited retrogradation. Nevertheless, there is no conclusive mechanism defining how sugars interacted with starch molecules.

Degree of starch retrogradation can be determined by X-ray diffraction pattern or by measuring increased gel firmness. More recently, DSC has been applied by some researchers to study starch retrogradation (Nakazawa et al 1984, 1985; Eliasson 1985; Russell 1987; Chang and Liu 1991; Kohyama and Nishinari 1991; Wang et al 1992), as well as glass transition temperature of carbohydrate (Levine and Slade 1986, 1988; Roos and Karel 1990, 1991a,b; Kalichevsky and Blanshard 1992; Karmas et al 1992; Liu and Lelievre 1992; Roos 1993). However, there has not much been done on relating T_g' with starch retrogradation. The purpose

of this study was to investigate the effect of T_g' on starch retrogradation during storage at different temperatures by using DSC.

MATERIALS AND METHODS

Sample Preparation

Corn starch (Sigma Chemical Co., St. Louis, MO), sugars, and maltodextrin of 10 dextrose equivalence (DE) (Grain Processing Corp., Muscatine, IA) were suspended in deionized ultrafiltered (DIUF) water (Fisher Scientific, Pittsburgh, PA) as mixtures of 20% (w/w) starch and 6 or 9% (w/w) sugars and maltodextrin. Sugars included glucose (anhydrous, Fisher Scientific), fructose (Sigma), maltose (monohydrate, Grade 1, Sigma), and sucrose (Fisher Scientific). The slurry was mixed with a Vortex mixer (Fisher Scientific), then 12–15 mg of the homogenous solution was transferred into aluminum DSC pans, sealed, and equilibrated for at least 1 hr before analysis. Maltodextrin of 6, 9, 26, 29, and 40% concentrations were also prepared.

DSC

The T_g' , as well as the enthalpies of gelatinization and retrogradation of starch, maltodextrin, starch-sugar, and starch-maltodextrin mixtures were determined by using a Perkin-Elmer DSC7 analyzer equipped with an Intracooler II system (Perkin-Elmer Corp., Norwalk, CT). The instrument was calibrated with cyclohexane for low temperature and with indium for high temperature. An empty pan was used as the reference. Samples were first heated from 25°C to 100°C (10°C/min) to complete gelatinization before the T_g' was determined. Gelatinized samples were stored at 2°C or -20°C in a commercial refrigerator. Enthalpy of retrogradation and T_g' were measured every seven days for 21 days.

The T_g' of samples after gelatinization and after storage were determined following the method of Roos (1993). Samples were initially scanned from -70°C to 25°C to locate T_m' , the onset temperature of ice melting in a maximally freeze-concentrated solution. Samples were then cooled to -70°C (30°C/min), heated to $T_m' - 1^\circ\text{C}$ (10°C/min), annealed for 15 min at $T_m' - 1^\circ\text{C}$, cooled to -70°C (10°C/min), and scanned from -70°C to 25°C (5°C/min) to determine T_g' and T_m' . After T_g' and T_m' were determined, enthalpy of retrogradation was measured by scanning the samples from 25°C to 100°C (10°C/min). The analog derivative function on the DSC7 equipment allowed precise determinations of T_g' with a reproducibility of $\pm 0.5^\circ\text{C}$. The peak temperature of the glass transition thermogram was taken as the T_g' , and the onset temperature of the ice-melting thermogram was considered as the T_m' (Fig. 1). Each measurement was performed in triplicate.

Gel-Permeation Chromatography (GPC)

The molecular size distribution of maltodextrin 10 DE was elucidated by using GPC. The procedure followed that of Jane and Chen (1992) with modification by Wang et al (1993). Fifteen milligrams of maltodextrin was dissolved in 5 ml of distilled water. The solution was loaded onto a Sepharose CL-2B column (2.6 i.d. \times 95 cm) (Pharmacia LKB Biotech, Uppsala, Sweden). Effluent fractions of 5 ml were collected and subjected to total carbohydrate assay by the anthrone-sulfuric acid method (Wright and Gann 1966).

RESULTS AND DISCUSSION

T_g' and T_m' of Starch Mixtures

The T_g' and T_m' of starch, sugars, maltodextrin, starch-sugar, and starch-maltodextrin mixtures are listed in Table I. The results for starch, sugars, and maltodextrin agreed with the values reported by Levine and Slade (1986, 1988). Because solute concentration in a maximally freeze-concentrated matrix is about 80% (Roos and Karel 1991b), any solute concentration below 80% exhibited the same T_g' . A 20% starch solution was chosen as a reference, and 6 and 9% glucose concentrations were chosen so that the T_g' of the mixture was close to the T_f (-20°C). The

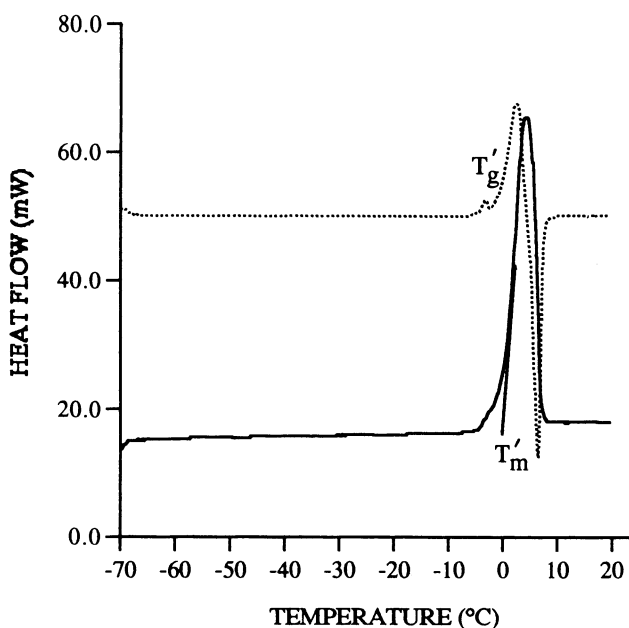


Fig. 1. Differential scanning calorimetry thermogram for 20% (w/w) of starch. T_g' = specific glass transition temperature. T_m' = temperature at which ice melts. Heat flow (—). Derivative trace (.....).

same concentrations were used for the rest of the sugars and maltodextrin. Our preliminary results showed that annealing was necessary to achieve maximal freeze-concentration with constant T_g' and T_m' , which was in accordance with findings of Roos and Karel (1991a), but was not reported by Levine and Slade (1986). Results showed that as the amount of sugars in starch-sugar mixtures increased, the T_g' and T_m' decreased (Table I). The LMW molecules decreased the T_g' of mixtures more than the HMW molecules, and maltodextrin did not decrease the T_g' as other sugars did because of its relatively high T_g' (Levine and Slade 1986, 1988).

Starch Retrogradation During Storage

Table II summarizes the retrogradation percentage of different starch mixtures stored at 2°C or -20°C for different time periods. Retrogradation percentage is defined as the ratio of retrogradation enthalpy to gelatinization enthalpy (Wang et al 1992). There were no significant differences among samples stored at 2°C, except

that those samples with 6 and 9% fructose after 21 days and those with 6 and 9% maltodextrin after 14 and 21 days exhibited greater retrogradation. The results indicated that glucose, maltose, and sucrose at concentrations of 6 and 9% neither increased nor prevented starch retrogradation at 2°C storage. This disagrees with previous reports (Maxwell and Zobel 1978, Germani et al 1983, l'Anson et al 1990, Chang and Liu 1991, Kohyama and Nishinari 1991). The discrepancy may result from the difference in the proportion of starch to sugar used in different studies or from the different storage conditions, such as temperature. The samples were unstable under the storage conditions used in this study (2°C) because the T_g' was lower than 2°C (Table I). Therefore, all mixtures showed similar retrogradation rate with or without the sugars and maltodextrin. By measuring the gel rigidity, Maxwell and Zobel (1978) reported a marked acceleration in starch crystallization on wheat starch gel with added fructose when compared with the addition of glucose or sucrose. Our results showed that fructose did not accelerate starch retrogradation for up to 14 days of storage, but it accelerated significantly at the end of 21 days.

The addition of maltodextrin increased starch retrogradation at 2°C. To verify that the increased retrogradation was contributed by maltodextrin, the retrogradation of maltodextrin alone at different concentrations and the MW distribution of maltodextrin were studied. The storage results are summarized in Table III, and the GPC elution profile of the maltodextrin is presented in Figure 2. The results showed that at high concentration (40%), maltodextrin itself caused retrogradation at 2°C after seven days storage, but at low concentrations (6, 9, 26, and 29%), retrogradation did not occur after 21 days. The HMW molecules of maltodextrin could reassociate to form double helices among themselves or with starch molecules. Therefore, at low maltodextrin concentration, the presence of starch may help the reassociation of HMW molecules of maltodextrin. Maltodextrins are widely used to increase viscosity, to retard crystallization, and to decrease the stickiness and hygroscopicity of dried materials (Levine and Slade 1988). However, the retrogradation of maltodextrin might add to the total amount of retrogradation when antecedents are added into starchy foods.

TABLE I
Glass Transition Temperatures (T_g') and Onset Temperatures of Ice Melting (T_m') in the Maximally Freeze-Concentrated Solutions

Solution Composition (w/w)	T_g'	T_m'
20% Starch	-3.2	0.5
20% Glucose	-40.3	-6.0
20% Fructose	-42.5	-6.1
20% Maltose	-28.3	-3.2
20% Sucrose	-32.2	-3.4
20% Maltodextrin	-11.1	-0.6
20% Starch + 6% Glucose	-17.1	-2.2
+ 9% Glucose	-22.5	-3.2
+ 6% Fructose	-18.2	-1.9
+ 9% Fructose	-22.2	-3.1
+ 6% Maltose	-12.3	-1.1
+ 9% Maltose	-14.8	-1.8
+ 6% Sucrose	-14.3	-1.2
+ 9% Sucrose	-16.4	-2.2
+ 6% Maltodextrin	-4.7	0.3
+ 9% Maltodextrin	-5.5	-0.6

TABLE II
Retrogradation Percentage^a of Starch, Starch-Sugar, and Starch-Maltodextrin after Storage at 2°C and -20°C

Sample	ΔT (°C) ^b	2°C Storage (%)			-20°C Storage (%)		
		7 Days	14 Days	21 Days	7 Days	14 Days	21 Days
20% Starch	-16.8	50 ± 1	55 ± 2	59 ± 1	0 ± 0	3 ± 0	7 ± 3
+ 6% Glucose	-2.9	50 ± 2	56 ± 1	58 ± 1	22 ± 2	30 ± 2	39 ± 3
+ 9% Glucose	2.5	46 ± 1	57 ± 1	57 ± 1	35 ± 2	42 ± 1	46 ± 4
+ 6% Fructose	-1.6	49 ± 4	55 ± 1	65 ± 1	31 ± 1	41 ± 4	45 ± 3
+ 9% Fructose	2.4	53 ± 1	56 ± 2	66 ± 2	41 ± 3	53 ± 1	57 ± 2
+ 6% Maltose	-7.7	41 ± 1	50 ± 3	55 ± 2	6 ± 4	6 ± 4	8 ± 2
+ 9% Maltose	-5.2	42 ± 0	50 ± 2	59 ± 1	6 ± 1	7 ± 1	10 ± 0
+ 6% Sucrose	-5.7	42 ± 1	50 ± 2	56 ± 3	7 ± 6	10 ± 4	17 ± 1
+ 9% Sucrose	-3.6	46 ± 0	52 ± 3	56 ± 1	8 ± 2	14 ± 3	17 ± 2
+ 6% Maltodextrin	-15.3	46 ± 1	63 ± 2	72 ± 1	4 ± 4	10 ± 2	17 ± 2
+ 9% Maltodextrin	-14.5	51 ± 1	71 ± 1	78 ± 3	10 ± 2	13 ± 5	15 ± 7

^aRatio of enthalpy of retrogradation to enthalpy of gelatinization. Values (average ± standard deviation) are calculated from three determinations.
^b $\Delta T = T_f - T_g'$, where $T_f = -20^\circ\text{C}$ and T_g' are listed in Table I.

TABLE III
Retrogradation^a of Maltodextrin after Storage at 2°C and -20°C

Maltodextrin in Sample (%)	T_g' (°C) ^b	2°C Storage (J/g)			-20°C Storage (J/g)		
		7 Days	14 Days	21 Days	7 Days	14 Days	21 Days
6	-11.4	0	0	0	0	0	0
9	-11.1	0	0	0	0	0	0
26	-11.2	0	0	0	0	0	0
29	-11.1	0	0	0	0	0	0
40	-10.9	0.5 ± 0.2	1.1 ± 0.1	1.7 ± 0.2	0	0	0

^aValues (average ± standard deviation) are calculated from three determinations.
^bSpecific glass transition temperature. Standard deviations are ± 0.5°C.

Samples stored at -20°C exhibited significantly less retrogradation compared with those stored at 2°C . Samples with no sugars exhibited less than 10% retrogradation after 21 days of storage. Those with maltose, sucrose, and maltodextrin exhibited about 20% retrogradation. Samples with glucose and fructose exhibited more than 20% retrogradation after seven days of storage and reached more than 40% after 21 days. Fructose accelerated starch retrogradation more than any other sugar, regardless of the storage condition.

The T_f (-20°C) was lower than the T_g' of samples with no sugars and samples with maltose, sucrose, and maltodextrin, which resulted in good storage stability. Levine and Slade (1986) proposed that the stability of frozen foods was controlled by the temperature difference (ΔT) between T_f and T_g' of the matrices ($\Delta T = T_f - T_g'$). The higher the T_g' of the mixtures, the greater the storage stability of foods. The T_g' of the mixtures could be increased through formulation by adding HMW molecules, such as low DE maltodextrins. In this study, samples with maltodextrin had a much higher T_g' than those with maltose and sucrose. However, they exhibited similar degrees of retrogradation. The discrepancy can be attributed to the additional amount of retrogradation from HMW maltodextrin.

Samples with 6% glucose and 6% fructose had a T_g' slightly above the T_f and were supposed to be stable at -20°C storage. However, they showed 22 and 31% retrogradation after seven storage days. The low stability may be attributed to the fact that

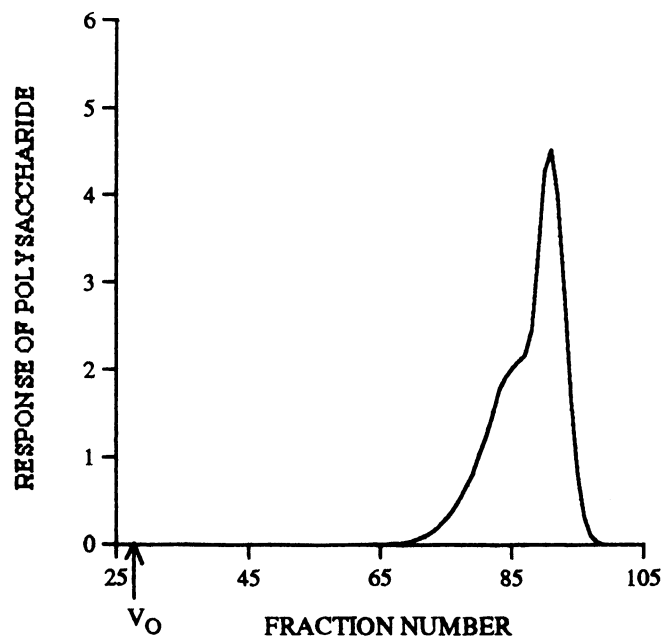


Fig. 2. Gel-permeation chromatography elution profile of maltodextrin 10 DE on Sepharose CL-2B column. V_0 is the void volume.

the commercial freezer used in this study has defrost cycles, which perhaps interrupted the constant T_f . Another possibility is that T_g' consists of a temperature range rather than a specific temperature. Kalichevsky et al (1992) suggested that the glass transition was not observed at a specific temperature, but was related to the frequency and nature of the measurement technique after they investigated the glass transition of amylopectin (waxy maize) by using DSC, dynamic mechanical thermal analysis (DMTA) and nuclear magnetic resonance (NMR). Thereafter, different T_g' were reported, depending on researcher techniques.

Also, it is possible that the T_g' of individual components, in addition to the T_g' of the mixture, play a role in determining the stability of food. In this study, the T_f was higher than the T_g' of the samples with 9% glucose and fructose but lower than the T_m' of glucose and fructose. For samples with 9% glucose and fructose stored at -20°C , the glucose and fructose molecules existed in a rubbery state instead of a glassy state like starch because the T_f was between the T_g' and T_m' of glucose and fructose (Levine and Slade 1986, 1988). The movement of glucose and fructose molecules is possible in the rubbery state, which facilitates the movement of starch molecules, and thus, the reassociation and retrogradation of starch.

Statistical analysis (data not shown) indicated that ΔT was significantly ($P < 0.01$) correlated with starch retrogradation for samples stored at -20°C for 7, 14, and 21 days with $r = 0.79$, 0.77 and 0.74, respectively. No significant correlation was found for samples stored at 2°C . This confirmed the use of ΔT as an indicator to predict the storage stability of frozen foods (Levine and Slade 1986). However, the T_g' of individual components should be taken into consideration as well, especially those with LMW.

T_g' Change During Storage

T_g' of starch-sugar mixtures varied with storage. Individual T_g' of stored samples are listed in Table IV. In general, samples stored at 2°C had higher T_g' than those stored at -20°C (except with maltodextrin) for the same composition and the same period of time. The change of T_g' varied from -0.7°C to $+4.4^{\circ}\text{C}$ for samples containing sugars and maltodextrin stored at 2°C for 21 days, and -0.4°C to $+3.7^{\circ}\text{C}$ for samples stored at -20°C . No significant T_g' change was found for starch samples with no sugars under either condition. It is plausible that some sugar was absorbed or included in retrograded starch after storage, but most of the sugar remained in the unfrozen solution portion. In turn, the decreased sugar concentration in the remaining solution increased the T_g' of the mixture. A greater T_g' increase was found in samples stored at 2°C because sugars in solution were mobile and able to interact with starch. In contrast, less sugar-starch interaction was allowed for samples stored at -20°C ; therefore, T_g' increase was less pronounced. As storage time proceeded, more and more sugars became involved with retrograded starch or were absorbed and removed from the solution, which increased the T_g' also. Those with no sugars showed no T_g' increase. The starch-maltodextrin mixture showed an opposite effect: the

TABLE IV
Specific Glass Transition Temperature (T_g') of Individual Samples Stored at 2°C and -20°C ^a

Sample	T_g' ($^{\circ}\text{C}$)	2°C ($^{\circ}\text{C}$)			-20°C ($^{\circ}\text{C}$)		
		7 Days	14 Days	21 Days	7 Days	14 Days	21 Days
20% Starch	-4.0	-4.5	-4.5	-4.5	-3.7	-3.7	-3.6
+ 6% Glucose	-17.1	-16.3	-15.4	-14.8	-17.3	-16.8	-15.6
+ 9% Glucose	-22.5	-19.7	-19.2	-18.1	-19.9	-19.5	-19.6
+ 6% Fructose	-18.4	-15.9	-15.5	-15.4	-16.7	-16.4	-15.3
+ 9% Fructose	-22.4	-19.6	-19.6	-18.0	-20.4	-20.5	-18.7
+ 6% Maltose	-12.3	-10.6	-11.2	-10.4	-12.1	-11.5	-11.6
+ 9% Maltose	-14.8	-13.0	-12.9	-12.1	-14.4	-13.9	-12.6
+ 6% Sucrose	-14.3	-11.5	-11.0	-11.6	-12.9	-13.0	-12.8
+ 9% Sucrose	-16.4	-13.8	-13.6	-13.5	-15.3	-15.1	-15.1
+ 6% Maltodextrin	-4.7	-4.8	-4.8	-5.4	-4.9	-5.2	-5.1
+ 9% Maltodextrin	-5.5	-5.6	-5.5	-6.0	-5.9	-5.8	-5.5

^a Values are the average of three determinations. Standard deviations for all samples are $\pm 0.5^{\circ}\text{C}$.

T_g' decreased slightly after storage. This could be attributed to the preferential retrogradation of HMW maltodextrin, resulting in an increased proportion of small molecules in the amorphous solution.

Spies and Hosney (1982) proposed that sugars bonded with starch chains in the amorphous regions, thus producing interactions between starch chains. This study also suggested that sugars were absorbed and, thus, did not contribute to the shift of T_g' .

Fructose-containing samples exhibited the greatest T_g' increase during storage, suggesting more fructose could be absorbed by starch molecules when compared to other sugars. How sugars interact differently with starch is not clear. Fructose may fit better into the starch molecule conformation without interfering with starch reassociation. The T_g' shift to a higher temperature helped to stabilize the system and to decrease retrogradation by decreasing ΔT .

The T_g' increase during storage shown in this study suggests that although the T_g' of mixture is used for predicting storage stability, the T_g' may not remain constant, depending on individual components and storage conditions.

CONCLUSION

Starch samples with fructose exhibited greater retrogradation than did those with glucose, maltose, and sucrose at both 2°C and -20°C storage conditions. Samples containing 9% fructose had the highest degree of retrogradation (57%) at -20°C after 21 days of storage. Maltodextrins, although they will improve the storage stability through increasing composite T_g' , may contribute a certain degree of retrogradation to starchy foods. The T_g' did not remain constant, but shifted to a higher temperature during storage for samples with added sugars. In contrast, samples with no sugars showed similar T_g' throughout storage. The results confirmed that the lower the temperature difference between T_f and the composite T_g' ($\Delta T = T_f - T_g'$), the greater the stability of frozen foods.

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