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Comparison in glass transition and enthalpy relaxation between native and gelatinized rice starches

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Abstract

Native and gelatinized rice starches were compared in their glass transition and enthalpy relaxation at various water contents using a differential scanning calorimetry (DSC). In a low moisture content range (8–18%), the glass transition temperature (T_g) of native starch was higher (up to 20°C) than that of gelatinized starch, and the difference became greater as the moisture content decreased. Heat capacity change (ΔC_p) at T_g became substantially higher by gelatinization. Plasticizing effect of water on the glass transition in the low moisture content range followed the Couchman–Karasz equation. The glass transition temperature ($T_g{}'$) of native starch with sufficient moisture (40 or 60%) also appeared higher (−6.8 or −6.0°C) than that of gelatinized starch (−10.0 or −7.7°C), but ice-melting occurred in broader temperature range with smaller ΔH when the starch was gelatinized. Upon extended storage up to 14 days at 4°C, the gelatinized starch showed increased $T_g{}'$ but decreased ice-melting enthalpy due to the water incorporation in recrystallization of starch. Enthalpy relaxation appeared only when the moisture was $<20\%$ regardless of gelatinization. The relaxation peak increased in magnitude as the moisture content increased, and appeared as 'T_g overshoot' at a moisture content above 12% due to superimposed glass transition, whereas at a moisture content below 12%, it located in a temperature range far below glass transition, showing a 'sub-T_g endotherm'. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Glass transition; Enthalpy relaxation; Rice starch

1. Introduction

Starch is biosynthesized as water-insoluble granules in which crystalline regions are interspersed amongst continuous amorphous matrix (French, 1984). Melting of the crystallites is a first-order transition that shows changes in enthalpy, entropy and volume, whereas glass transition of the amorphous regions is a second-order transition that shows a discontinuous change in heat capacity (Roos, 1995).

At a sufficiently low temperature or limited content of plasticizer, molecular motion becomes restricted as a glassy solid is formed. On heating or plasticizer addition, the mobility of the amorphous polymers increases and the material becomes flexible or rubbery. Thus, the glass transition denotes a change from brittle to rubbery behavior at a temperature T_g. The T_g depends on molecular characteristics, composition and compatibility of the components in the amorphous matrix (Fox & Flory, 1950; Gordon & Talyor, 1952; Kalichevsky & Blanshard, 1992; Roos & Karel, 1991a), and this is obvious in complex systems such as foods and biomaterials. The glass transition behavior affects any types of food properties related to the molecular mobility including texture and shelf-life (Levine & Slade, 1993; Mizuno, Mitsuiki & Mitoki, 1998).

If a starch gel or paste where moisture is sufficient is progressively cooled, ice crystallization often causes the solid concentration and viscosity of the starch/water liquid phase to increase because some water remains unfrozen (Blond & Simatos, 1998). Franks, Asquith, Hammond, Skaer and Echlin (1979) initially referred to the glass transition temperature of this freeze-concentrated liquid phase as $T_g{}'$, and it has been known as a threshold of instability for solute/water systems which could be an important parameter for the quality and stability of frozen food systems (Roos, Karel & Kokini, 1996; Simatos & Blond, 1993). The glass transition of frozen starch/water dispersion occurs several degrees below ice melting, and devitrification (ice recrystallization) often accompanies this transition (Roos, 1995).

Many studies have been reported on the glass transition behavior of a variety of starch-water systems. However, studies on the T_g of starch, either in a high moisture or

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limited moisture range, have mostly been made after the starch crystals are destroyed because of the difficulty in analyzing T_g in the native semicrystalline state (Biliaderis, 1991; Biliaderis, Page, Maurice & Juliano, 1986; Blond & Simatos, 1998; Liu & Lelievre, 1992; Roos et al., 1996; Thiewes & Steeneken, 1997; Vodovotz & Chinachoti, 1998; Zelenznak & Hoseney, 1987). There are several reasons why the T_g of native starch could be different from destructured starch. Firstly, the crystalline domains are surrounded by the continuous amorphous regions in starch granules, and thus they behave like cross-linkages to the amorphous regions, suppressing amorphous chain mobility. Secondly, intercrystalline amorphous phases, which may have a mixed structure between pure crystalline and amorphous structures, can exist in the starch granule, and thus the amorphous transition is not clearly independent from the crystalline melting. Thirdly there may be significant heterogeneity in the amorphous structure in native starch granules, possibly due to the mixed composition of amylose and amylopectin both of which have a high polydispersity and constituents of the amorphous regions (Biliaderis, 1991; Biliaderis et al., 1986; Thiewes & Steeneken, 1997; Zelenznak & Hoseney, 1987).

The sub-T_g endotherm is often observed at low moisture contents on the DSC thermogram, also causes difficulty in T_g analysis (Shogren, 1992; Thiewes & Steeneken, 1997; Yuan & Thompson, 1994). This phenomenon was referred to enthalpy relaxation, enthalpy recovery, or structural relaxation (Hodge, 1994). Kalichevsky, Jaroszkiewicz, Ablett, Blanshard and Lillford (1992) identified this calorimetric feature in amylopectin/water mixtures, and simply described it as a low temperature transition. It has also been suggested as representation of a structural relaxation in the glassy state of starch (Noel, Ring & Whittam, 1993). The feature is not observed on the thermogram after immediate reheating but generally re-appears upon storage (Gidley, Cooke & Smith, 1993; Noel et al., 1993), indicating its time-dependent characteristics toward the equilibrium of a glassy state (Appelqvist, Cooke, Gidley & Lane, 1993; Gidley et al., 1993; Noel et al., 1993; Shogren, 1992).

The objectives in this study are to explore the glass transition and enthalpy relaxation of rice starch as a function of water content, and to compare these transitions between native and gelatinized states of the starch.

2. Materials and methods

2.1. Materials

Rice starch was isolated from a Japonica-type rice flour by following the procedure of Chung, Cho, Chung, Shin, Son and Lim (1998). Purified rice starch was prepared in amorphous state by dissolving the isolated starch in dimethyl sulfoxide (DMSO), followed by precipitation with ethanol (Jane & Chen, 1992).

2.2. Preparation of DSC samples

Thermal transition of rice starch was measured at various moisture contents. The starch sample (30 ± 0.1 mg dry solid basis) was placed in a silver DSC pan (70 μl) and then distilled water was added until the starch was fully wet. The water was allowed to evaporate in a balance until the desired moisture content was reached, and then the pan was hermetically sealed. The moisture content was calculated by measuring weight of the sealed pan. For the experiment with limited moisture, the moisture content was adjusted to 8–18% (w/w), and for that with excess moisture, it was adjusted to 40 or 60%. The amorphous rice starch purified in DMSO was hydrated in a humidity chamber over distilled water to a moisture contents of 14–16%.

2.3. Differential scanning calorimetry (DSC)

The T_g and enthalpy relaxation (sub-T_g endotherm) were measured using a differential scanning calorimeter (Seiko Instrument, DSC6100, Chiba, Japan). The instrument was calibrated with indium and mercury (156.6 and −39.0°C for melting, respectively).

At a limited moisture content (8–18%), enthalpy relaxation in native starch was characterized by heating the DSC sample from 5 to 85°C at a heating rate of 2°C/min. The sample was immediately cooled to 5°C at 20°C/min with liquid N_2, and then reheated at 2°C/min for the measurement of glass transition. During the initial measurement, both enthalpy relaxation and glass transition appeared together, without disruption of starch crystals, but only a glass transition appeared in the reheated thermogram. The T_g was determined as the peak point on the first derivative curve of the heat capacity thermogram.

At a high moisture content (40 and 60%), the starch–water mixture which had been equilibrated for 1 h at room temperature was rapidly cooled to −60°C at 20°C/min, and then heated to 45°C at 2°C/min for the determination of the $T_g{}'$.

To measure the thermal transition of gelatinized rice starch, the DSC pans containing starch and water were preheated using the instrument until starch melting was completed. Heating up to 200°C was required for the complete melting for the sample containing limited moisture (8–18%), whereas the starch with high moisture content (40 or 60%) was gelatinized by heating to 160°C. The gelatinized sample was immediately cooled to 5°C at 20°C/min, and then reheated at 2°C/min until the enthalpy relaxation and glass transition were measured.

2.4. Storage

The DSC sample pans containing 40 or 60% moisture were stored for 14 days at 4°C. The sample pans of low moisture content (8–18%) were stored at 25°C for 5 days.

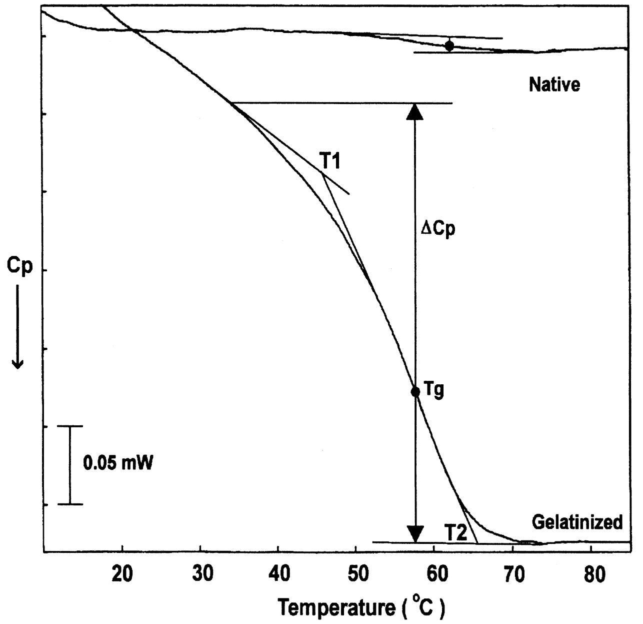

Fig. 1. DSC thermogram for glass transitions of native and gelatinized rice starches at 14% moisture content.

The changes in both transitions during storage were periodically measured.

3. Results and discussion

3.1. Glass transition at low moisture content

When the moisture is limited, structural relaxation in glassy starch occurs, and the corresponding endotherm often interferes the measurement of the T_g. Because this relaxation is time-dependent, the T_g can be solely observed by an immediate rescanning of the heated samples (Thiewes & Steeneken, 1997; Zelenznak & Hoseney, 1987). The reheated thermograms, showing the reversed glass transition of native and gelatinized rice starches at 14% moisture, are shown in Fig. 1. It was revealed that the T_g and ΔC_p at T_g were distinctively different between native and gelatinized states from the same rice starch. The glass transition of native rice starch produced very small ΔC_p, whereas that of the corresponding gelatinized starch exhibited substantially higher ΔC_p. Native rice starch is partially crystalline (38% crystallinity) as reported in a literature (Roos, 1995), and thus the magnitude of the amorphous regions is lower by this portion than gelatinized starch. The difference in the amorphous portion could be the major reason for the ΔC_p difference.

As the moisture content increased from 8 to 18% (w/w), the ΔC_p at T_g increased from 0.020 to 0.072 J/g°C for native starch, and from 0.123 to 0.213 J/g°C for gelatinized starch. This trend was due to the increased plasticizing effect of water, which gives more free volume to starch chains (Noel & Ring, 1992; Roos, 1995).

As shown in Fig. 1, the glass transition on the DSC thermogram appeared asymmetric, in the sense the heat flow at the beginning and end of the transition were not in same magnitude. This phenomenon became more obvious when the starch was gelatinized. Wunderlich (1990) suggested six parameters to characterize the calorimetric glass transition: onset and end temperatures for the transition (T_o and T_e), extrapolated onset and end temperatures (T_1 and T_2), glass transition temperature (T_g), and heat capacity change (ΔC_p). For the gelatinized rice starch at 14% moisture, these values were 35, 72, 46, 65, 57°C and 0.182 J/g°C, respectively (Fig. 1). The T_g measured from the first derivative curve did not correspond to the midpoint in ΔC_p, which was an indication of the asymmetric transition. It was supposed that, in either native or gelatinized starch-water matrix, multiple amorphous segments possibly different in size and structure exist, and the segmental motion of the amorphous starch chains is slowly initiated from local side chains before the entire polymer backbone in the amorphous regions acquires its mobility. Therefore, the progressive increases in chain mobility results in an increase in the rate of the transition causing an asymmetry heat flow.

The T_g of anhydrous starch could not be determined experimentally due to the thermal decomposition of starch. Nakamura and Tobolsky (1967) estimated the T_g by extrapolation, and reported a relatively high value (330°C) for anhydrous amylose. Orford, Parker, Ring and Smith (1989) predicted T_g of both anhydrous amylose and amylopectin to be 227 ± 10°C. Whittam, Noel and Ring (1990) determined T_g of anhydrous starch at 297°C. Roos and Karel (1991b) reported that the T_g of anhydrous starch was estimated to be 243°C based on the Fox and Flory equation. The experimental data in this study fitted the Couchman–Karasz equation (ten Brinke, Karasz & Ellis, 1983; Couchman & Karasz, 1978). The T_g and ΔC_p at T_g of pure water are −139°C and 1.94 J/g°C, respectively (T_{g2} and ΔC_{p2}), and from the equation the estimates of T_g and ΔC_p of anhydrous native rice starch were 296°C and 0.285 J/g°C, and those of gelatinized rice starch were 180°C and 0.500 J/g°C, respectively. It should be noted that the anhydrous T_g value was significantly different (over 100°C) between native and gelatinized rice starches.

$$T_g = \frac{w_1 \Delta C_{p1} T_{g1} + w_2 \Delta C_{p2} T_{g2}}{w_1 \Delta C_{p1} + w_2 \Delta C_{p2}} \qquad (1)$$

In the equation w_1,w_2 are the weight fractions of solids and water, ΔC_{p1}, ΔC_{p2} the heat capacity changes at their glass transition temperatures, and T_{g1},T_{g2} are the glass transition temperatures of solid and water respectively.

The trend in T_g depression by moisture, in native and gelatinized starches, clearly revealed that the T_g difference between native and gelatinized starches became greater when the moisture content was lowered (Fig. 2). And the difference was not noticeable at water content higher than

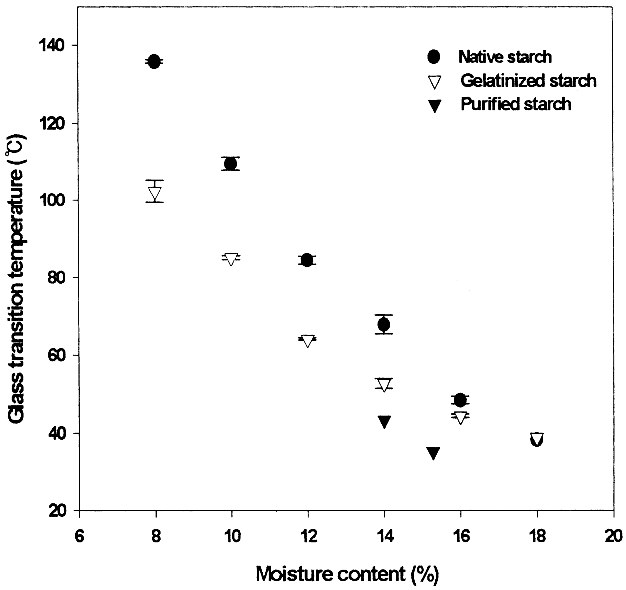

Fig. 2. Glass transition temperature (T_g) in native, gelatinized and purified rice starches.

18% (w/w). The T_g difference between native and gelatinized starches was reported first by Zelenznak and Hoseney (1987) for wheat starch. The crystalline regions suppress the mobility of the amorphous molecules because they behave as cross-linkages between the amorphous regions of a polymeric network (ten Brinke et al., 1983). The larger difference in T_g and ΔC_p between native and gelatinized starches at lower moisture content indicates that the constraining effect of crystallites is reduced by the presence of water which acts as a plasticizer.

When the granular structure of starch was chemically melted in DMSO, and recovered in an amorphous solid by ethanol, the T_g of the amorphous starch was even lower than that of the gelatinized starch at the same moisture contents (14–16%, Fig. 2). The purified starch by DMSO/ethanol contained only amorphous structure like the gelatinized starch, but this result shows that the thermal transition of amorphous starch can be affected by preparation procedure or thermal history.

3.2. Glass transition and ice melting at high moisture content

Fig. 3 shows the DSC thermogram regions for T_g' and ice melting of native and gelatinized rice starches containing 40 or 60% water. In the first derivative curves of the thermograms (B and D in Fig. 3), the glass transition behavior of the two different states of rice starch appeared clearly different. Gelatinized starch showed lower T_g' value but greater heat flow change at the T_g' than native starch. This result was similar to the data observed when water was limited (Fig. 1).

The T_g' changed widely from −4.7 to −10.0°C according to the moisture content and the storage period (up to 14 days at 4°C) (Table 1). The T_g' of the fresh native starch was −6.8 or −6.0°C, respectively at the moisture contents of 40 and 60%. These values were 2–3°C higher than those of the corresponding gelatinized starch, and the difference remained almost constant during storage. The higher water content (60%) resulted in a higher T_g'. As the storage period increased, T_g' was increased in both native and gelatinized starches. The T_g' increase was greater at 60% moisture than 40%. A similar observation of the T_g' increase at different moisture contents was made by Huang, Chang, Chang and Lii (1994). At the beginning of storage, native starch showed a relatively small difference in T_g' (0.8°C) between the two water contents (40 and 60% w/w), but the T_g' difference became more significant as the storage period increased (Table 1). The gelatinized starch showed a higher difference (2.3°C) even at the beginning of storage.

Glass transition in a freeze-concentrated phase depends upon ice formation. In a starch-water matrix, enthalpy and temperature for ice melting changed with storage time. The peak temperature of ice melting endotherm (T_m) was higher at the higher moisture content (60%), and this could be expected by the freezing temperature depression by the solutes. Several works (Roos, 1995; Roos & Karel, 1991a; Roos et al., 1996; Slade & Levine, 1991) have shown that T_g' is largely independent of initial water content, whereas T_m of ice is not. The experimental data in this study, however, showed that T_g' could also be changed by the moisture content change. For fresh native rice starch, T_m difference between 40 and 60% moisture contents was 0.5°C but it was greater (2.9°C) for the gelatinized starch. The greater susceptibility of the gelatinized starch to water content than native starch might be related to the greater quantity and mobility of the amorphous starch chains due to the absence of crystallites. The melting enthalpy of ice, which indicated the freezable water, was reduced by gelatinization (Table 1). Presumably because there is a greater proportion of amorphous chains to interact with water.

Both T_g' and ice melting T_m increased as the storage continued, regardless of gelatinization. Wang and Jane (1994) stored gelatinized corn starch and water mixture (1:4) for 7 days at 2 and −20°C, and found that T_g' decreased from −4.0 to −4.5°C on the storage at 2°C, but increased from −4.0 to −3.7°C at −20°C. After seven days, however, no further change occurred. Vodovotz and Chinachoti (1998) claimed that the T_g' increase during cold storage was due to amylopectin recrystallization. Under the storage conditions used in this experiment, the gelatinized starch recrystallized to give a melting enthalpy of 6–8 J/g during the storage for 14 days at 4°C (Table 1). When starch recrystallizes, some water molecules are incorporated in the crystalline lattices (Ablett, Darke, Izzard & Lillford 1993), and this causes a decrease in the freezable water in the matrix. The reduced mobile water causes the increases in T_g' and T_m (Table 1). Additionally, the newly formed starch crystal lattices facilitate the inter-locking effects of the amorphous chains, raising the glass transition

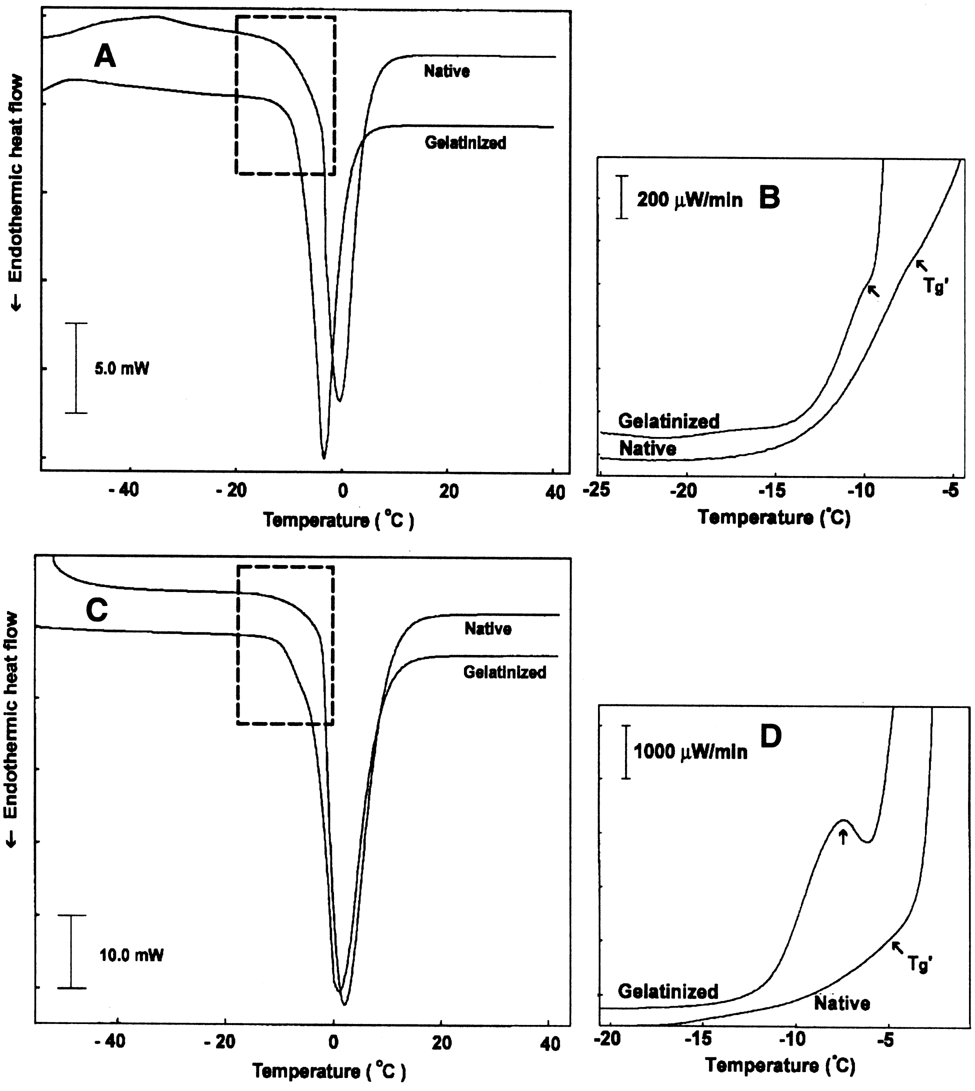

Fig. 3. DSC thermogram for glass transition temperature (T_g') of the unfrozen matrix in native and gelatinized rice starches (A: T_g' at 40% moisture content, B: first derivative of square dot line in A, C: T_g' at 60% moisture content, D: first derivative of square dot line in C).

temperature. The crystalline structure in native rice starch has an intact A type structure which contains four water molecules per 12 anhydrous glucose residues. But the new crystals formed from the gelatinized starch has B-type structure which contains 36 water molecules per 12 glucose residues (Zobel, 1992). Therefore, even a small degree of retrogradation is effective in reducing the freezable water content.

Native starch also displayed a reduction in ice melting enthalpy but an increase in starch melting enthalpy

Table 1

Glass transition temperature (T_g'), peak temperature (T_m) for ice melting and enthalpy for melting and starch meltings of native or gelatinized rice starch-water mixture (40 or 60% moisture) during the storages for 0, 7, and 14 days at 4°C[a]

Starch	Moisture content	T_g' (°C)			T_m for ice melting (°C)			ΔH for ice melting (J/g)			ΔH for ice melting (J/g)		
		0	7	14	0	7	14	0	7	14	0	7	14
Native	40	-6.8^{b}	-6.5^{a}	-6.3^{a}	0.4^{b}	0.7^{ab}	0.9^{a}	152.0^{a}	148.4^{b}	143.2^{c}	18.1^{b}	18.7^{b}	21.0^{a}
	60	-6.0^{b}	-5.7^{b}	-4.7^{a}	0.9^{b}	1.7^{a}	1.7^{a}	480.7^{a}	472.8^{ab}	454.3^{c}	17.1^{b}	17.2^{b}	19.6^{a}
Gelatinized	40	-10.0^{a}	-9.9^{a}	-9.9^{a}	-2.4^{b}	-1.7^{a}	-1.7^{a}	115.6^{a}	103.5^{b}	98.7^{c}	0.0	8.3^{a}	8.3^{a}
	60	-7.7^{b}	-6.9^{a}	-6.9^{a}	0.5^{b}	1.1^{a}	1.2^{a}	457.2^{a}	441.0^{b}	430.6^{c}	0.0	6.3^{a}	7.0^{a}

[a] Values of different alphabets indicate significant difference ($P < 0.05$) among the storage days (0, 7, and 14 days).

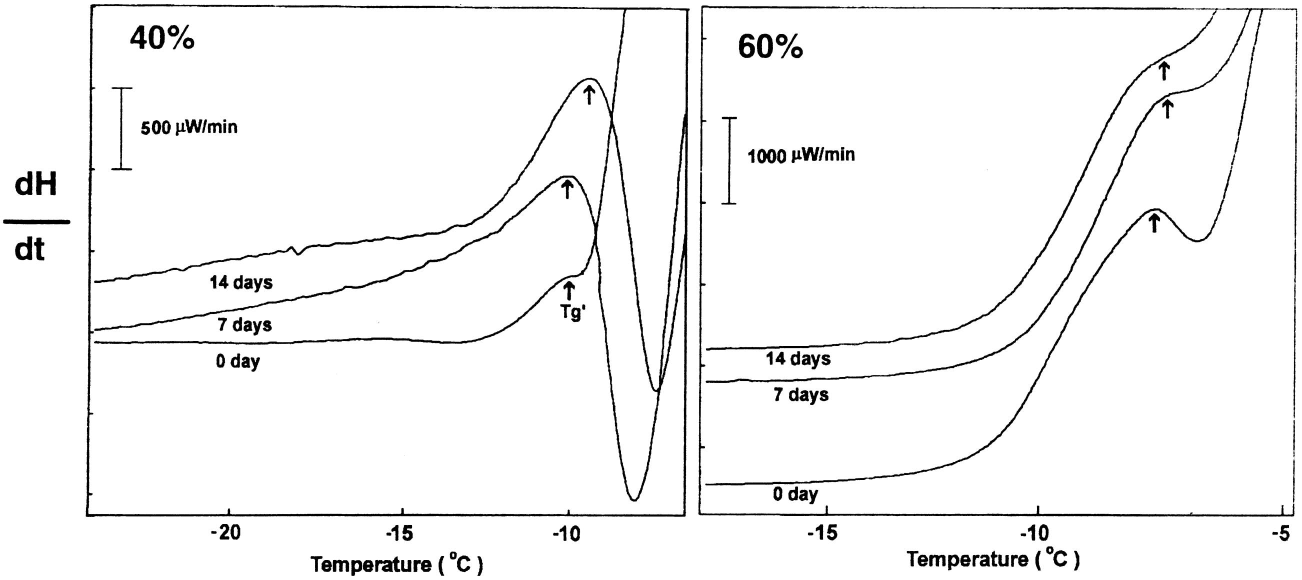

Fig. 4. First derivative of DSC themogram of the gelatinized rice starch containing 40 or 60% moisture content stored at 4°C up to 14 days.

during storage, although these changes were not so significant as found with the gelatinized starch (Table 1). This result suggests that native starch underwent a structural change during storage, presumably defined as an annealing process. Annealing caused minor increases in glass transition ($T_g{}'$) and ice melting temperatures (T_m) (Table 1). The freezable water content could be also changed by the annealing. Annealing did not affect crystalline structure (A type), but increased degree of crystallinity. However, the retrogradation changes the crystalline structure of rice starch to B-type (Eliasson & Gudmundsson, 1996). Therefore, freezable water in starch changes more significantly during retrogradation than during annealing due to the difference in crystalline type.

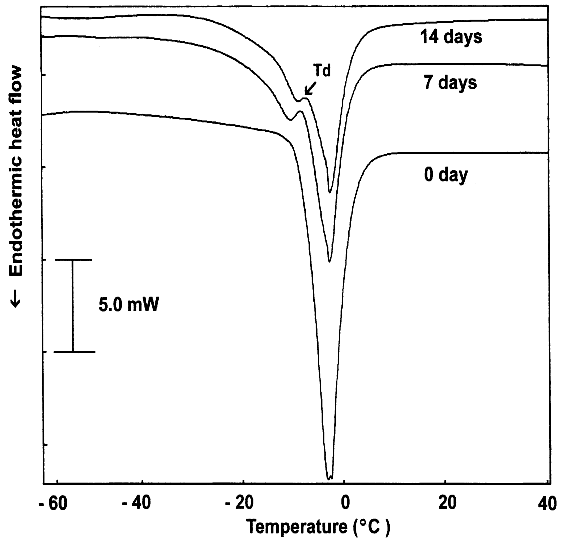

Fig. 5. DSC result of the gelatinized rice starch gel (40% moisture content) stored at 4°C up to 14 days (arrow indicates divitrification).

The overall data in this experiment revealed that the $T_g{}'$ of the concentrated starch-water matrix in frozen state was strongly dependent both of ice-forming behavior of the system as well as of starch recrystallizaiton.

Fig. 4 shows the derivative of the thermograms of gelatinized starch (40 or 60% water) at different storage periods. The gelatinized starch containing 60% water showed a distinctive peak at $T_g{}'$ at the beginning, but it became difficult to locate the $T_g{}'$ as the storage time increased because of the gradual decrease in ΔC_p. The derivative curve at 40% moisture showed a different pattern. The starch sample stored for 7 or 14 days displayed the intensified peak on the curves and the sharp drop in dH/dt right after the glass transition. This change was caused by an exothermic transition that occurred immediately after the glass transition (Fig. 5). The exotherm was attributed to the crystallization (devitrification) of unfrozen residual water. At the glass transition, starch chains in the freeze-concentrated liquid phase acquired mobility, and the chain movement initiated water crystallization in the supercooled system. Huang et al. (1994) claimed that the magnitude of the devitrification increased as the moisture content decreased, and at a moisture content over 50% the exotherm was not detectable. Liu and Lelievre (1992) reported that, in a gelatinized starch–water mixture (45% starch), the devitrification exotherm appeared clearly when the sample was quickly frozen, but it became absent when the sample was stored at room temperature for a week. However, it has been reported that the exotherm was observed when a wheat starch gel containing 48% moisture was stored for seven days at 4°C (Vodovotz & Chinachoti, 1998). Therefore, the appearance of the exotherm for ice formation is dependent of the

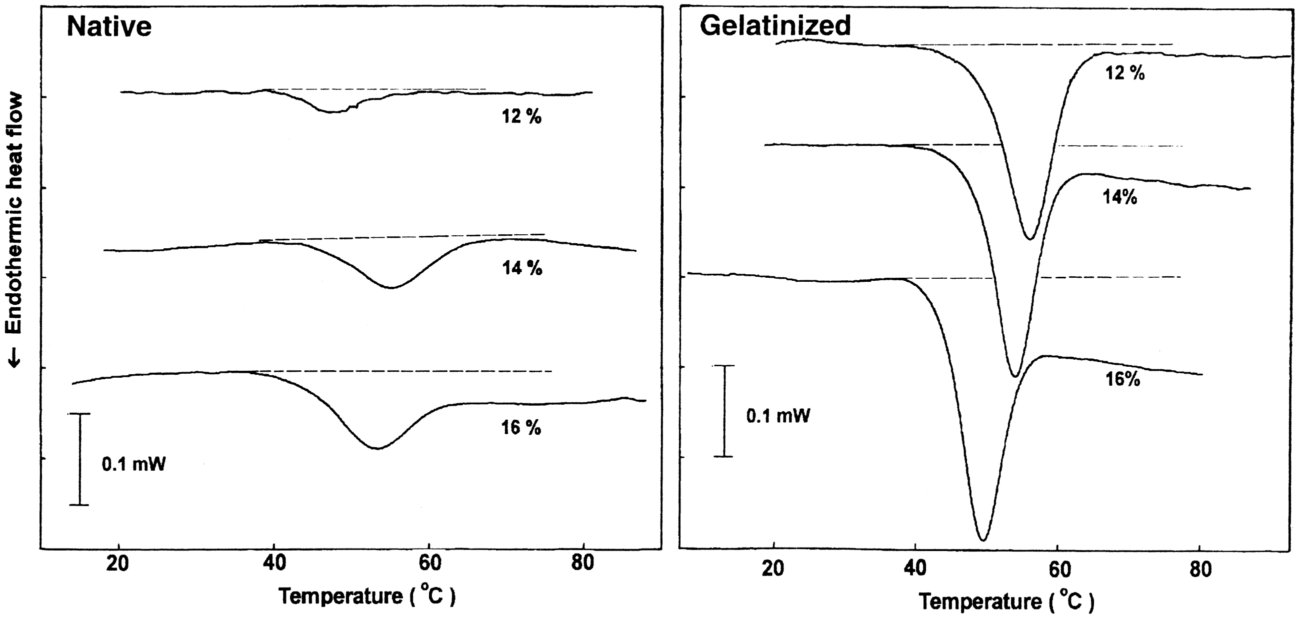

Fig. 6. DSC thermogram for glassy enthalpy relaxation after subtraction of glass transition of native and gelatinized rice starches at low moisture content (12–16%).

thermal history and storage conditions of the starch, as well as of the thermal analytical conditions.

Solid concentration in the maximally freeze-concentrated phase ($C_g{}'$) was estimated from the state diagram to be 74.7% for native starch, and 72.8% for the gelatinized starch (diagrams not shown). Our values of $T_g{}'$ and $C_g{}'$ were in good agreement with those reported in literatures (−5 to −11°C and 73%, respectively) (Jouppila & Roos, 1997; Roos & Karel, 1991b; Slade & Levine, 1988). It was noteworthy that the $C_g{}'$ for native starch measured in this experiment was 2% higher than that for gelatinized starch. This result indicates that the gelatinized starch contains more unfreezable water than native starch. This conclusion is supported by the pervious discussion in which the gelatinized starch chains are more effective in immobilizing the liquid water molecules than the starch chains orderly arranged in native granule. And the larger amount of unfrozen water led to the lower $T_g{}'$ for the gelatinized starch sample (Table 1).

As indicated in Fig. 3 and Table 1, the ice melting in the gelatinized starch sample appeared as a broader endotherm but a lower enthalpy than that native starch sample. Liu and Lelievre (1992) have already reported that the ice melting became broader in the presence of starch matrix, and this trend was facilitated further by water-immobilization by the starch chains in the gelatinized sample. The water-immobilization rendered the inhibitory effect on water-crystallization, leading to a reduced amount of freezable water. The decrease in ice melting enthalpy by starch gelatinization was in agreement with the $C_g{}'$ difference between native and gelatinized starch samples.

3.3. Enthalpy relaxation

A structural relaxation in glassy amorphous regions, displayed as an endothermic peak, was observed in both native and gelatinized rice starch samples in this experiment. For comparison between native and gelatinized starches, the endothermic peak was measured after the starch samples were initially heated to remove the relaxation endotherm and then aged for one day at 25°C to regenerate the endotherm. The aged starch sample provided the thermogram containing glass transition and relaxation endotherm. The glass transition was eliminated by subtracting the reheated thermogram (Fig. 6) (Montserrat, 1994; Schimidt & Lammert, 1996).

Kalichevsky et al. (1992) reported that the endothermic enthalpy varied proportionally to moisture content and not affected by lipid presence in starch. The purified rice starch in DMSO and ethanol was tested in a separate experiment, and it showed an endotherm similar to that observed by the gelatinized starch (data not shown). Therefore, it was confirmed that this transition was not originated from the impurities in commercial starch, but it was a genuine thermal characteristic of starch.

In order to examine the effect of starch origin, native starches from potato and corn were tested at an equal moisture content of 15% in a preliminary experiment. The T_p (peak temperature) and enthalpy for the endotherm were 45.6°C and 0.50 J/g for potato starch, and 47.2°C and 0.60 J/g for corn starch, respectively. These values seemed slightly different from those of native rice starch (46.0°C, 0.52 J/g), but the difference was not statistically significant. We suppose that there is little dependency on the origin of the starch.

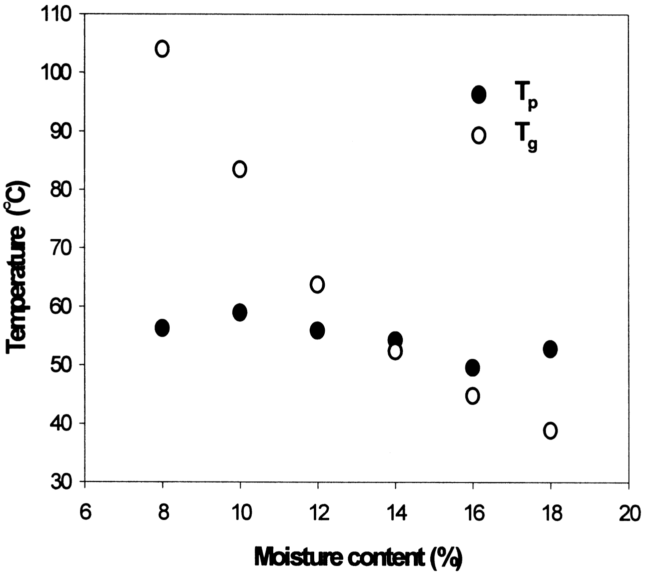

Fig. 7. Peak temperature of enthalpy relaxation (T_p) and T_g in gelatinized rice starch at different moisture contents (8–18%).

Native rice starch exhibited an endothermic enthalpy lower than that of the gelatinized starch and the temperature range for the native starch endotherm was broader (Fig. 6). Because the endotherm represents the structural relaxation in a glassy amorphous polymer matrix, it could be expected that the enthalpy was positively related to the magnitude of the amorphous fraction. The higher enthalpy for the endotherm in gelatinized starch might result from the raised quantity of amorphous matrix by gelatinization. However, in native starch, the crystalline micelles might cause the broadening of the endotherm due to their inter-locking effect among the amorphous regions.

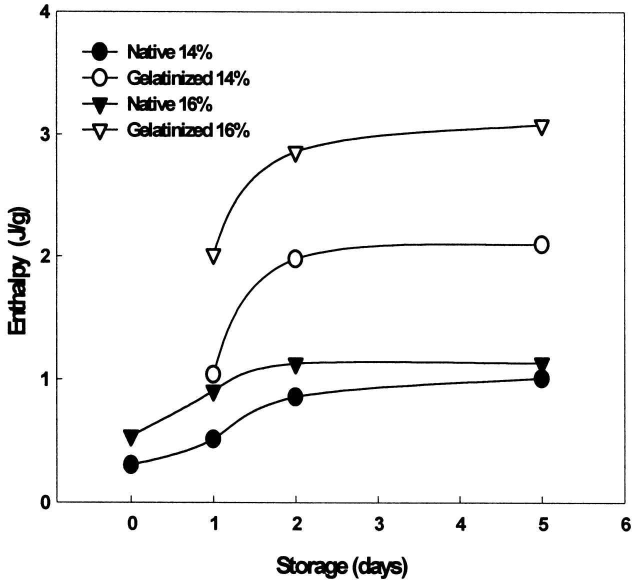

Fig. 8. Enthalpy change of the endothermic relaxation during storage with 14 and 16% moisture contents in native and gelatinized rice starches.

The endotherm appeared symmetric on the DSC thermogram in which glass transition had been eliminated, but the baseline shifted downward after the transition (Fig. 6). The baseline shift was more significant as the moisture content increased. The baseline shift by the endothermic transition may be caused by two possible phenomena: (1) the endothermic transition forms a new structure which has a different C_p; (2) the ΔC_p at T_g in the first and second scanning is not equal. Although the glass transition is theoretically reversible, the aging may cause the ΔC_p difference. The mobility increase by moisture may change the ΔC_p at T_g as indicated in Fig. 6.

The relaxation endotherm temperature (T_p) and glass transition temperature (T_g) of the gelatinized starch at different moisture contents are shown in Fig. 7. The relaxation temperature showed no moisture-dependency, whereas the T_g decreased as the moisture content increased. Therefore, when the residual moisture content was low, the relaxation endotherm appeared far below T_g. In this case, the endothermic peak appeared not overlapping glass transition on thermogram, and was often referred as 'sub-T_g peak'. However, it approached the glass transition as the moisture content increased because the T_g decreased rapidly. When the moisture content was above 14%, T_p of the relaxation peak surpassed the T_g within glass transition range (Fig. 7). When the endotherm superimposed on the T_g, it is often called 'T_g overshoot'. This was observed above 14% moisture in this experiment. The T_g overshoot and sub-T_g peak in synthetic polymers have been carried out by changing the aging temperature (Montserrat, 1994; Mukherjee & Jabarin, 1995; Muzeau, Vigier & Vassoille, 1994). Montserrat (1994) suggested that the peak temperature of endotherm (T_p) of epoxy resins increased when the aging temperature (T_a) was near T_g. But T_p was constant, when T_a was $T_g - 10$°C. This was because the system was near its structural equilibrium at the aging temperature. He also showed that T_p could appear surpassing T_g as shown in our results. However, in our starch-systems, T_g continually decreased as the moisture content increased whereas T_a remained constant.

The relaxation endotherm is not thermally reversible but dependent of aging. Both native and gelatinized rice starches with limited moisture (14 or 16%) were aged up to five days at 25°C after removal of the original endotherm. The magnitude of the endotherm increased rapidly during the early stage (up to two days), but the enthalpy change became minor thereafter (Fig. 8). A similar result has been reported by Gidley et al. (1993). For the relaxation of epoxy resin, Montserrat (1994) reported that ΔH became constant when the aging was carried out for about 24 h at 90°C (T_g 98.3°C). Mukherjee and Jabarin (1995) found a longer equilibrium period (41 days) for poly(ethylene terephthalate) (PET) on aging at 40°C (T_g 78°C). Schimidt and Lammert (1996) obtained constant enthalpy with glassy maltose by aging for three days at 30°C (T_g 43.1°C). These results indicate that the period reaching relaxation equilibrium is

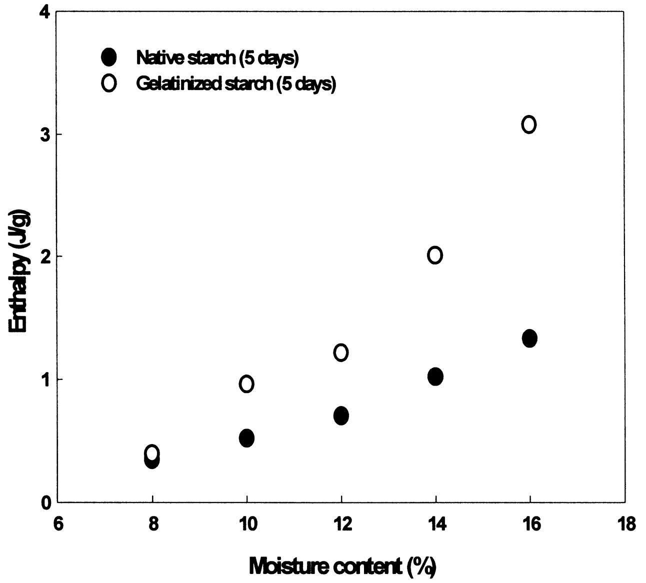

Fig. 9. Enthalpy change of the endothermic relaxation at different moisture contents (<20%) in native and gelatinized rice starches.

greatly affected by the nature of polymers and the difference between T_g and T_a ($T_g - T_a$). Fig. 8 additionally shows the moisture dependency of ΔH for native and gelatinized rice starches. The gelatinized starch showed a higher sensitivity to the moisture content (14 or 16%) compare to native starch.

The relaxation enthalpy at a near equilibrium state (five days aging) was also compared at different moisture contents (8–16%) between native and gelatinized rice starches (Fig. 9). Although the T_p appeared independent to the moisture content (Fig. 7), the enthalpy for the relaxation proportionally increased with the residual moisture content (Fig. 9). This trend has been already reported by many researchers using gelatinized starch (Appelqvist et al., 1993; Gidley et al., 1993; Kalichevsky et al., 1992; Shogren, 1992; Yuan & Thompson, 1994). It was observed in this experiment that gelatinized starch showed a steeper increase in enthalpy on raising moisture content than native starch. This could be another phenomenon manifesting that gelatinized starch has higher susceptibility to moisture than native starch. Moreover, this phenomenon could be explained by the fact that the amorphous fraction is responsible for the aging phenomena.

Shogren (1992) described the enthalpy relaxation with a statement that, when a short-range rearrangement in a glassy polymer structure was induced by thermal energy, the structure became relaxed and mobile, giving a peak in C_p. And an additional increase in C_p was followed as a rearrangement of entire amorphous polymers, the point of which was called as T_g. This theory was based on the concept that endothermic relaxation preceded the glass transition. He also interpreted the enthalpy increase by raised moisture content as a result from the increased relaxation rate of the glassy state due to water-induced local mobility. This phenomenon was claimed to be dependent on $T_g - T_a$ (difference between glass transition temperature and aging temperature). This theory by Shogren agrees somewhat with the experimental data when the endotherm appeared as sub-T_g peak (separation from T_g). However, the experimental data showing T_g overshoot could not be to explain in this theory. It is

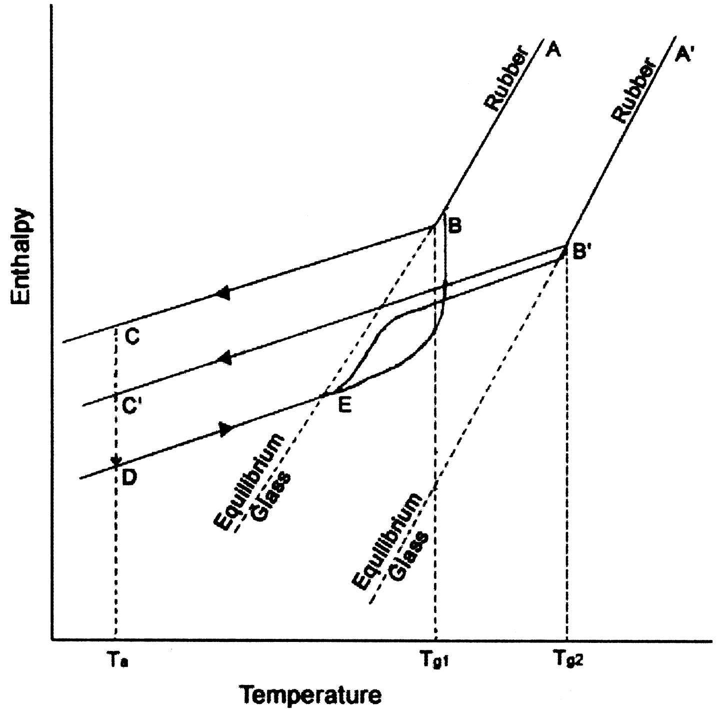

Fig. 10. Schematic diagram for the temperature-enthalpy relations of the rice starch-water samples with isothermal aging at T_a.

hypothesized, therefore, that the structure relaxation of the glassy polymer and the mobility increase of the entire amorphous polymers at T_g may be independent phenomena.

Gidley et al. (1993) and Yuan and Thompson (1994) claimed a different theory for the endothermic relaxation in which the endotherm represented the disruption of a hydrogen bonded network of starch and water, and the enthalpy increase by water was due to the higher chance for hydrogen bond formation. Yuan and Thompson (1994) reported that the endotherm disappeared after drying the starch samples to 2% moisture content, and thus the endotherm represented the melting of carbohydrate–water interaction. The claim that the water molecules participate in structure-formation in the amorphous phase through improvements in hydrogen bond agrees with the enthalpy increase with moisture content. However, the theory based on the carbohydrate–water interactions for the endotherm could not account for the disappearance of the peak at moisture content higher than 25%. Thiewes and Steeneken (1997) took an alternative view based on a two-stage aging experiment at different temperatures. They supposed that the endotherm for carbohydrate–water interactions had a constant enthalpy and temperature, regardless of thermal treatment. But starch samples aged at 70°C gave a different enthalpy and temperature on subsequent aging at 30°C.

The experimental data in this study revealed that the enthalpy for the endothermic relaxation depended on moisture content and aging condition. But the endotherm temperature was independent to moisture content, whereas the glass transition was dependent to moisture content. Therefore, the main difference between enthalpy relaxation and glass transition was their temperature dependences on the moisture content.

When a starch–water matrix is heated above T_g, starch chains attain a high free energy. Being subsequently cooled rapidly below T_g, the starch–water matrix returns in a non-equilibrium state. However, with aging, it relaxes to a lower enthalpy level. This enthalpy relaxation phenomenon may be explained on schematic diagram for the temperature-enthalpy relations based on our experimental data (Fig. 10) (Berens & Hodge, 1982). The starch sample cooled to an aging temperature (T_a, path ABC) relaxes along path CD with enthalpy change during a certain aging period. A subsequent heating at a relatively higher moisture content from 12 to 18% in our experiment, follows the path DEBA giving an endothermic peak superposed on the T_g (T_g overshoot). The starch containing a lower moisture content (8–12%) follows a different path A′B′C′ for cooling through a higher T_g, and the enthalpy relaxation(C′D) was less but reached to the same equilibrium point. The recovery started far below T_g at E in the diagram, following path DEB′A′. That relaxation peak appears as a sub-T_g peak separated from T_g.

The positive relation of the relaxation enthalpy to moisture content, not to the starch itself, can be explained in the diagram for enthalpy-temperature relations (Fig. 10). When the moisture content was high, the high-enthalpy state produced due to the increased free volume (different glass–rubber equilibrium line are attained with different moisture contents). The high-enthalpy consequently facilitates the relaxation process during aging. Therefore, the volume expansion induced by moisture was clearly consistent with this trend of the enthalpy dependency on moisture in our experiments.

The other possible change induced by moisture is transformation of starch chains toward specific structure. In the experimental moisture range, the residual water migrates into starch matrix to form thermally stable structure by direct interaction with starch chains. Under these stressful conditions due to the insufficient moisture, a minor increase of the moisture content may lead to a significant effect on the structure formation. This explains the moisture-susceptibility and the raised thermal stability by the structure transformation. But the detailed mechanism for the relaxation in the glassy state of starch has not been fully understood, and further study is required.

4. Conclusions

The amorphous regions in native granular and gelatinized rice starches showed substantially different thermal transition behaviors. This was more obvious when the moisture content in starch matrix was limited. At high moisture content (40 or 60%), the glass transition temperature in freeze-concentrated matrix (T_g') was slightly higher for native starch than gelatinized starch. But starch recrystallization or annealing with the help of water consumed the freezable water, and caused the T_g' to increase. The glass transition difference can be explained by the inter-locking effect of discontinuous crystallites as well as the magnitude difference in the amorphous phase.

The endothermic event of the glassy starch-water matrix at a limited moisture content (8–18% in this experiments), was facilitated by water, showing either T_g overshoot or sub-T_g peak. But the endothermic temperature appeared independent to the moisture in the tested range. The structural formation in the glassy state was time-dependent and nearly reached equilibrium after two days aging at 25°C.

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