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Physical aging of glassy normal and waxy rice starches: effect of aging temperature on glass transition and enthalpy relaxation

Hyun-Jung Chung, Seung-Taik Lim*

Graduate School of Biotechnology, Korea University, 1,5-ka, Anam-dong, Sungbuk-ku, Seoul 136-701, South Korea

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Abstract

Effect of physical aging at different temperatures (T_a) on the amorphous transitions of normal and waxy rice starches has been investigated using differential scanning calorimetry (DSC). Glass transition temperature (T_g) increased, but ΔC_p at the T_g decreased, as the difference ($T_g - T_a$) between T_g and T_a increased, because the molecular mobility was reduced as the aging temperature was farther from T_g. The extent of relaxation was analyzed by determining the limiting relaxation enthalpy (ΔH_∞) at various aging temperatures. The ΔH_∞ versus $T_g - T_a$ revealed the two different roles by kinetic and thermodynamic controls for the relaxation. When $T_g - T_a$ was low ($0 \sim 30$ °C), ΔH_∞ increased with $T_g - T_a$, whereas when $T_g - T_a$ was high (above 30 °C), it decreased with $T_g - T_a$. At a constant $T_g - T_a$, the residual moisture raised ΔH_∞ due to plasticization effect. The effect of aging temperature on the relaxation temperature range was opposite to that on ΔH_∞, and the peak range became narrower as the moisture content increased. The ΔH_∞ and peak temperature range were different between normal and waxy rice starches. The normal rice starch had a higher ΔH_∞ and a narrower peak temperature range than did waxy rice starch.

Keywords: Physical aging; Glass transition; Enthalpy relaxation; Rice starch

1. Introduction

Physical aging is a phenomenon that has been regarded with great importance considering the storage behavior of glassy foods and pharmaceutical products (Borde, Bizot, Viber, & Buleon, 2002a,b; Champion, LeMeste, & Simatos, 2000). A glassy polymer, which is not in a thermal equilibrium, relaxes toward an equilibrium under a kinetic control. It is commonly referred to as physical aging or enthalpy relaxation (Struik, 1978). Aging affects a number of physical properties including density, modulus, enthalpy, and volume, the changes of which are often measured by using thermal analyzers such as differential scanning calorimeter (DSC) and dynamic mechanical thermal analyzer (DMTA). The DSC determines the enthalpy changes induced by structural rearrangement in glassy polymer. In our previous research (Chung & Lim, 2003), physical aging of rice starch was investigated using a DSC in terms of aging time. The waxy rice starch relaxed more rapidly than normal rice starch, and the relaxation process deeply depended on the $T_g - T_a$.

The enthalpy relaxation by aging, revealed by an endothermic peak in DSC thermogram, and the mechanical properties of the aged glassy polymer are clearly affected by aging temperature (Barral et al., 1999; Cowie & Ferguson, 1989; Monstrrat, 1992, 1994). Monsterrat (1992, 1994) investigated the aging phenomena of an epoxy resin at various aging temperatures, and reported that the maximum enthalpy relaxation (ΔH_∞) could only be determined experimentally when T_a was near T_g, approximately between T_g and 10 °C below T_g, and the aging time was too long to reach a structural relaxation equilibrium when T_a was less than $T_g - 10$ °C. They also suggested that the maximum enthalpy value decreased with aging temperature when T_a was greater than $T_g - 10$ °C. Cowie and Ferguson (1989) reported the aging phenomena of poly(vinyl methyl ether) in which the maximum enthalpy changed in a linear fashion with the difference between glass transition and aging temperatures ($T_g - T_a$), within the difference range of $8 \sim 21$ °C. Similar trends governed by $T_g - T_a$ have been reported by many researchers (Aref-Azar, Arnoux, Biddlestone, & Hay, 1996; Barral et al., 1999; Cook, Mehrabi, &

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* Corresponding author. Tel.: +82-2-3290-3435; fax: +82-2-927-5201.
E-mail address: limst@korea.ac.kr (S.-T. Lim).

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Edward, 1999). Hancok, Shamblin, and Zografi (1995) examined amorphous pharmaceutical solids, and found that the mean relaxation time was decreased by the increasing aging temperature (T_a).

Recently, Borde et al. (2002b) reported the physical aging characteristics of amorphous hydrated polysaccharides at various aging times and temperatures. They suggested that the enthalpy recovery (relaxation) was greater as the aging temperature was closer to glass transition temperature, whereas it was significantly reduced as the aging temperature was lowered. However, only few studies were carried out on the physical aging phenomena of polysaccharides in relations to the aging time and temperature. Enthalpy relaxation is an important phenomena occurring along storage of glassy starch products because they undergo physical change such as texture and brittleness required by the consumer. The understanding of enthalpy relaxation behavior in these products as function of temperature would be contributed to a better control during storage.

In our previous study (Chung & Lim, 2003), glass transition temperature, heat capacity change, fictive temperature, and enthalpy relaxation kinetics of rice starches as function of aging time were investigated. In the present study, those thermal characteristics related to the physical aging were investigated as a function of aging temperature for glassy normal and waxy rice starches.

2. Materials and methods

2.1. Materials

The normal and waxy rice starches were isolated from corresponding rice flours (Japonica type) purchased at a local grocery (Seoul, Korea) by using a dilute NaOH solution (Lim, Lee, Shin, & Lim, 1999), and purified in amorphous state using dimethylsulfoxide (DMSO) and ethanol (Jane & Chen, 1992).

2.2. DSC measurement

The amorphous rice starch (10 ± 0.1 mg dry solid basis) was placed in a silver DSC pan (70 °C), and then hydrated excessively in a humidity chamber over distilled water. The excess moisture was allowed to evaporate in a balance until desired moisture content (11, 13 or 15%) was reached, and then the pan was hermetically sealed. Prior to DSC analysis the starch sample was equilibrated at room temperature for one day.

Differential scanning calorimeter (Seiko Instrument, DSC 6100, Chiba, Japan), equipped with a refrigerated cooling accessory using liquid nitrogen, was used to measure the enthalpy relaxation and glass transition. Temperature and enthalpy values were calibrated with indium ($T_m = 156.6$ °C, $\Delta H_m = 28.590$ J/g) and mercury ($T_m = -39.0$ °C, $\Delta H_m = 11.472$ J/g), and heat capacity was calibrated with sapphire. An empty pan was used as the reference.

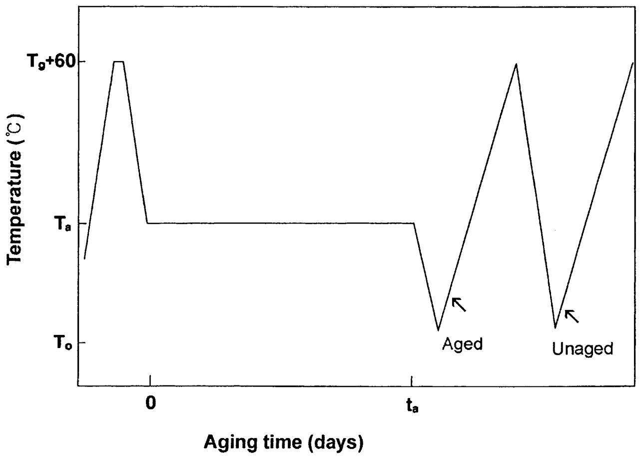

Fig. 1. Schematic diagram of thermal history for DSC experiments.

The glass transition temperature (T_g) was determined as the peak on the first derivative curve of the heat capacity thermogram.

2.3. Aging experiment

To perform the aging, the DSC sample was subjected to a thermal history as shown in Fig. 1. All samples were heated up to a temperature of approximately 60 °C above T_g ($T_g + 60$ °C) and held at that temperature for 10 min to erase previous thermal history. The starch sample was cooled to different aging temperatures at a cooling rate of 20 °C/min and aged at the temperature for 10 days. The difference between T_a and T_g ($T_g - T_a$) was a the range from 0 to 75 °C. After aging, the sample was immediately cooled to T_o (starting temperature, 5 °C) and scanned up to $T_g + 60$ °C (unaged sample) at a heating rate of 5 °C/min. The second scan was also made under the same heating and cooling conditions as for the unaged control. The measurements were done in triplicate.

3. Results and discussion

3.1. Glass transition temperature

The glass transition temperature (T_g) decreased substantially (by over 40 °C) as the moisture content increased from 11 to 15% (Fig. 2). The thermally induced starch chain mobility is very susceptible to the residual moisture when the plasticizing effect is limited (Ross, 1995; Slade & Levine, 1991). Regardless of moisture content and aging temperature, the T_g of normal rice starch was $3 \sim 5$ °C higher than that of waxy rice starch (Fig. 2). The difference in T_g between the amorphous normal and waxy rice starches has been already reported in our previous literature (Chung & Lim,

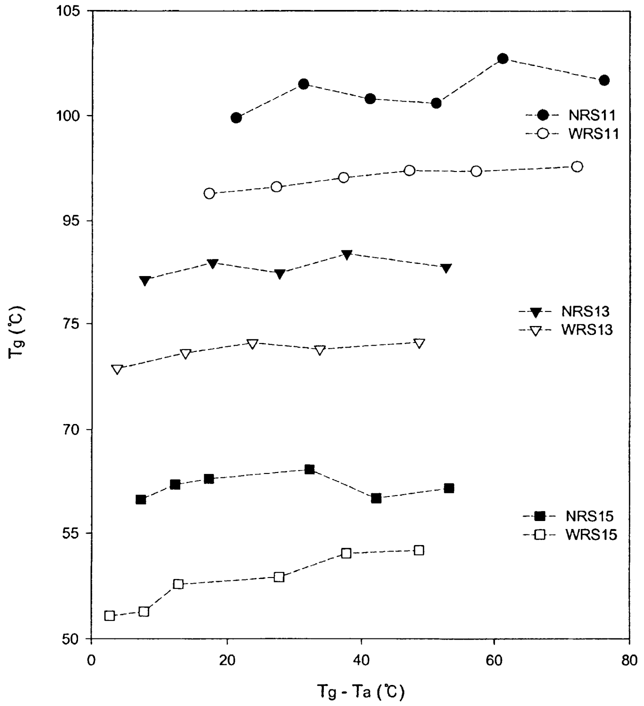

Fig. 2. Glass transition temperature (T_g) of normal and waxy rice starches with various aging temperatures.

2003). In the amorphous state where the inherent granular arrangements no longer exist, the restructurized conformation in the amorphous starch is dependent upon the starch purification and dehydration processes. The branching in waxy rice starch may hinder chain reassociation during the processes, whereas the presence of linear amylose facilitates formation of more rigid amorphous structure by the rapid chain association. Therefore, the normal rice starch displayed a higher T_g than did the waxy rice starch.

It was also found that the T_g appeared to increase as $T_g - T_a$ increased (as T_a decreased) (Fig. 2). This implies that the T_g of the starch decreased when the aging temperature (T_a) approaches T_g. This tendency may be explained using a schematic diagram of enthalpy against temperature as shown in Fig. 3 (Cerrada & McKenna, 2000). When a starch sample is quenched to an aging temperature ($T_1 \sim T_4$) below T_g without sufficient time to attain a thermodynamic equilibrium, it gradually relaxes by decreasing the enthalpy (H) and volume (V). However, as the aging temperature was closer to the T_g, the relaxation to an equilibrium (dotted line in Fig. 3) is faster due to higher segmental mobility of the starch chains. Consequently, the glass transition temperature ($T_{g1} \sim T_{g4}$), measured as intersection of the extrapolated lines, becomes much lower at a lower $T_g - T_a$ (e.g. T_{g4} for T_4 in Fig. 3).

3.2. Heat capacity increment

The heat capacity changes (ΔC_p) at T_g for the amorphous rice starch at different aging temperatures are given in Fig. 4. All starches tested were aged equally for 10 days. The normal rice starch showed higher ΔC_p than did the waxy rice starch, regardless of moisture content and aging temperature. In our previous work, similar result was observed when aging time was changed (Chung & Lim, 2003). It was hypothesized that the higher ΔC_p resulted from the heterogeneity in starch chain structure (amylose and amylopectin) in normal rice. The ΔC_p increase by increasing moisture content was from the increased mobility of the starch chains by the raised plasticization effect by moisture.

The ΔC_p of the aged normal and waxy rice starches was significantly influenced by $T_g - T_a$ when $T_g - T_a$ was less

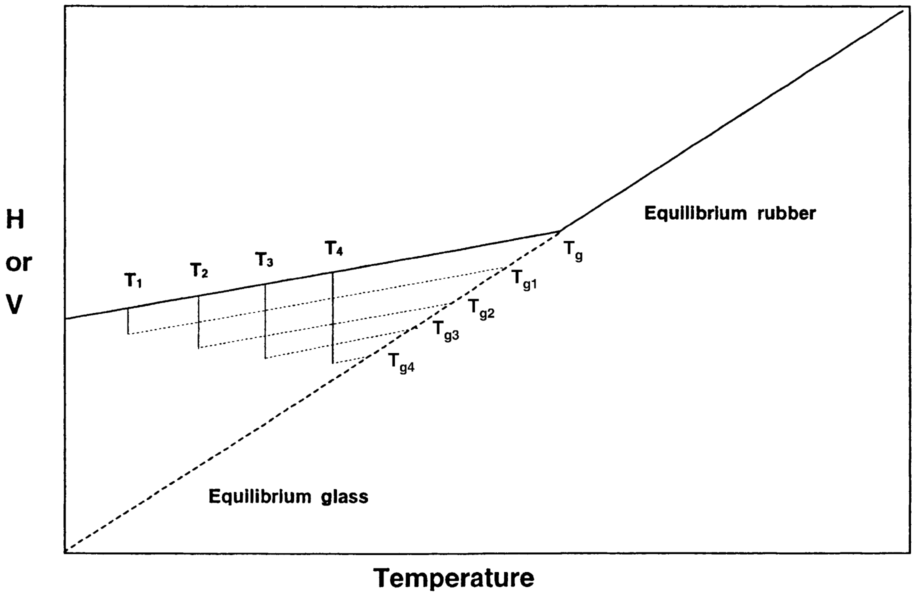

Fig. 3. Schematic of temperature versus enthalpy or volume for aging temperature effect on glass transition temperature (T_g).

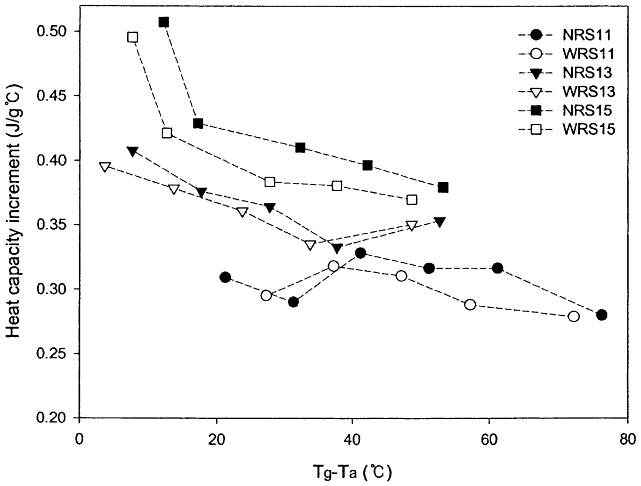

Fig. 4. Heat capacity increment (ΔC_p) at T_g of normal and waxy rice starches with various aging temperatures.

than 25 °C (Fig. 4). The free volume of starch was positively related to residual moisture content, but negatively related to aging time. This is a consequence of the decrease in the heat capacity (C_p) of the glassy state with aging time, but a constant C_p in the rubbery state ($\Delta C_p = \text{rubber } C_p - \text{glass } C_p$) (Borde et al., 2002a,b; Chung & Lim, 2003). During aging, the decreases in the volume and enthalpy of the glassy state were faster as the aging temperature was raised, because of the higher segmental mobility of polymer chains, and the decreased enthalpy was directly related to C_p in glassy state. Therefore, when the aging temperature becomes closer to T_g, the ΔC_p is raised due to the heat capacity decrease in the glassy state.

The ΔC_p of the aged starches slightly decreased as $T_g - T_a$ increased ($T_g - T_a > 25$ °C). In contrast, the decrease in volume and enthalpy with aging was slower when temperature $T_g - T_a$ was high and the extent of the volume and enthalpy decreases was lower when $T_g - T_a$ was higher than 25 °C. This process resulted in a minor change in the glass C_p with aging temperature. From the above results, it was concluded that the ΔC_p of amorphous rice starch at T_g depended on the aging temperature.

3.3. Enthalpy relaxation

The DSC thermograms of the normal rice starch containing 11% moisture at different aging temperatures are shown in Fig. 5. The location and intensity of the endothermic peaks varied with the aging temperature. When the $T_g - T_a$ was 50 °C or higher, the enthalpy relaxation peak became separated from T_g giving a sub-T_g peak, whereas it superposed on the T_g at a lower $T_g - T_a$ (30 and 40 °C) (T_g-overshoot). Chung, Lee, and Lim (2002) reported that the temperature range of the relaxation endotherm could be changed also by moisture content ($T_a = 25$ °C), showing a T_g-overshoot at a moisture content above 12%, but a sub-T_g peak at a moisture level below 12%. The $T_g - T_a$ at this moisture level (12%) was about 40 °C. In this experiment, also, shape of the relaxation endotherm changed at $T_g - T_a = 40$ °C for all the starch samples tested. This strongly suggests that the location of endothermic relaxation peak for starch depends strongly on $T_g - T_a$.

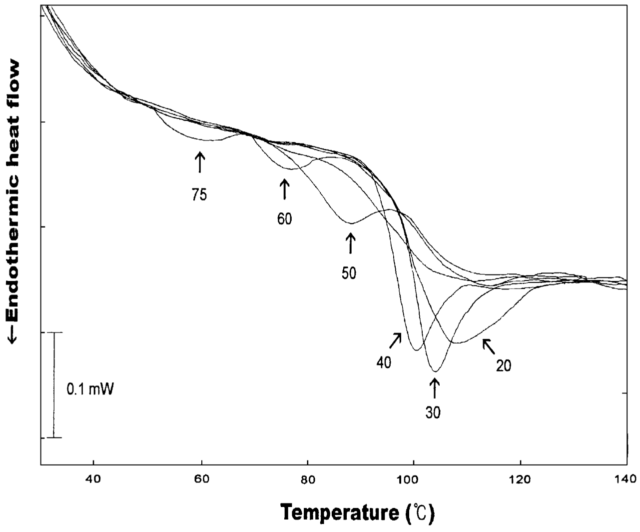

Fig. 5. DSC thermograms of normal rice starch at 11% moisture content with various aging temperature (The number indicate $T_g - T_a$).

The peak temperatures (T_p) of the enthalpy relaxation endotherm for the normal and waxy rice starches at different aging temperatures are given in Fig. 6. The T_p was inversely proportional to $T_g - T_a$ for all the moisture contents and starches tested. That is, the endothermic transition responsible for enthalpy relaxation occurs at a higher temperature range, as the aging temperature was higher. This trend agrees with other studies with waxy maize starch (Borde et al., 2002b) and with synthetic polymers (Barral et al., 1999; Berens & Hodge, 1982; Motserrat, 1994).

Based on the slope for T_p change against $T_g - T_a$, the T_p of relaxation endotherm was more susceptive to $T_g - T_a$

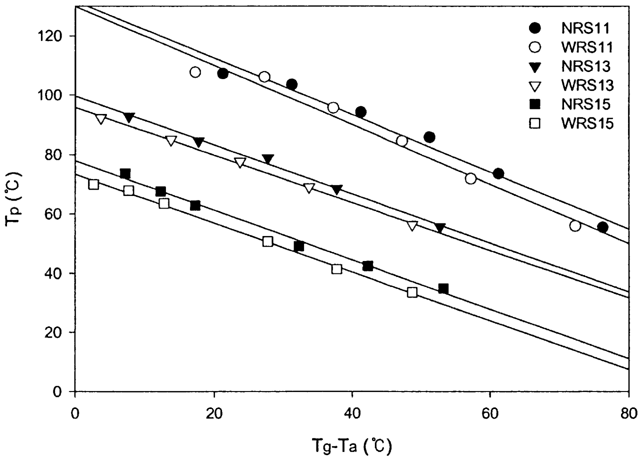

Fig. 6. The peak temperature of enthalpy relaxation versus $T_g - T_a$ of normal and waxy rice starches.

when moisture content was lower (e.g. 11%, Fig. 6). It indicates that the enthalpy relaxation may be more dependent on the aging temperature when the starch chains were less mobile (lower moisture content).

However, the experimental data revealed that the T_p measured at the three different moisture contents at constant T_a was relatively constant. Therefore, the endothermic peak temperature change was caused by the T_g change caused by differing moisture content. The T_p of normal rice starch was also higher than that of waxy rice starch (Fig. 6). This difference also was contributed by the T_g difference between normal and waxy rice starches (Fig. 2).

3.4. Physical aging kinetics

Physical aging kinetics of the amorphous rice starches were examined based on the maximum relaxation enthalpy (Fig. 7). In our previous study (Chung & Lim, 2003), the enthalpy (ΔH_∞) and aging time (t_c) for the maximum relaxation have been calculated from a non-linear curve fit using an equation of Cowie and Ferguson model (1986), and the values of t_c in rice starches were obtained as less than 10 days when T_a was below $T_g - 75$ °C. The aging period (10 days) used in the present experiment provided only a limited change towards an equilibrium, although continual but slow changes in enthalpy and volume were expected to be present. Thus, the aging time was fixed as 10 days, and the ΔH_∞ was measured at various aging temperatures.

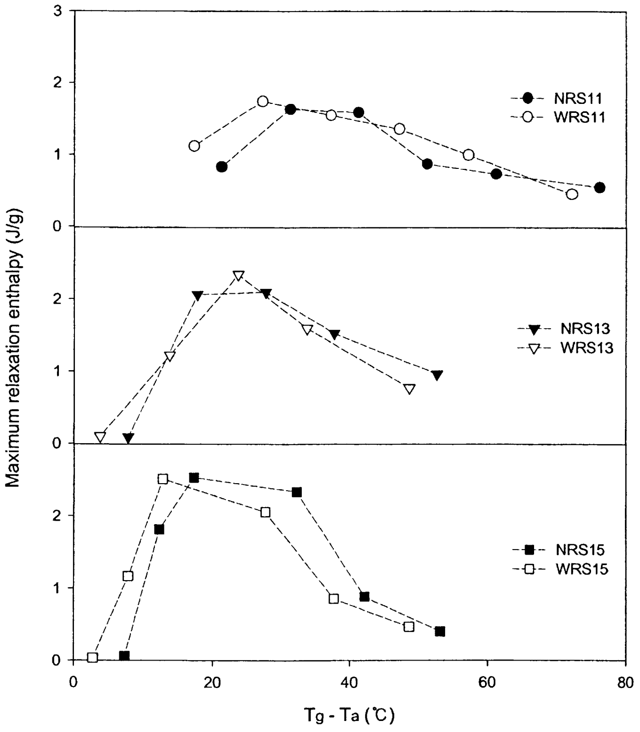

Fig. 7. The maximum relaxation enthalpy (ΔH_∞) versus $T_g - T_a$ of normal and waxy rice starches.

When the aging temperature was much less than T_g (high $T_g - T_a$), ΔH_∞ (maximum relaxation enthalpy) decreased as $T_g - T_a$ increased (Fig. 7). As the aging temperature increased approaching T_g (lowered $T_g - T_a$), however, the ΔH_∞ increased as $T_g - T_a$ increased. With these opposite trends, the ΔH_∞ change vs. $T_g - T_a$ results in forming a peak in the curve (Fig. 7), and this was observed similarly at the different moisture contents tested. Similar results were also reported by Montserrat (1994) and Cook et al. (1999) with epoxy resin. They claimed that this observation was caused by the different contributions of kinetics and thermodynamics to the aging phenomena. Over a wide $T_g - T_a$ range, reduction in molecular mobility results in a decreased rate of densification, and thus, within the time scale of the aging experiment, only a small loss of enthalpy occurs. When the aging temperature is raised in this $T_g - T_a$ range, the thermally enhanced molecular mobility facilitates starch densification. Thus the aging process is under kinetic control, resulting in a ΔH_∞ increase. However, at even higher aging temperature approaching T_g, the enthalpy of the glass is no longer different from that of the glass in the equilibrium state and so sample densification occurs only to a limited extent. Thus the aging process is now under a thermodynamic control in which the ΔH_∞ for relaxation decreases as the aging temperature increases toward T_g. Aref-Azar et al. (1996) reported that thermodynamic control applied when $T_g - T_a$ value was below $10 \sim 15$ °C, which agreed with data obtained in this experiment.

The slope ($\mathrm{d}\Delta H_\infty/\mathrm{d}T_g - T_a$) in the thermodynamic control range ($T_g - T_a < 20 \sim 30$ °C) was greater when the residual moisture content was higher (Fig. 7). The ΔH_∞ change in this range followed the following equation (Aref-Azar et al., 1996; Montserrat, 1994):

$$\Delta H_\infty = \Delta C_p(T_g - T_a) \tag{1}$$

in which a linear dependency of ΔH_∞ to $T_g - T_a$ based on ΔC_p, and positive relationship between ΔC_p to moisture content were revealed in agreement with our results (Fig. 7). Cook et al. (1999) suggested that the aging of an epoxy resin was retarded when highly crosslinked, and ΔC_p decrease caused this phenomenon. On the other hand, the ΔH_∞ drop in the range under kinetic control ($T_g - T_a > 30$ °C) was more substantial when the moisture content was higher (Fig. 7), but the rate of ΔH_∞ drop was relatively smaller than that under thermodynamic control. This result was consistent with the report by Cook et al. (1999) and Montserrat (1994). The relations in the kinetic control can be applicable by modifying the previous equation as follow:

$$\Delta H_\infty = -(\Delta C_p/3)(T_g - T_a) \tag{2}$$

In Fig. 7, at the same $T_g - T_a$, the ΔH_∞ of normal rice starch was higher than that of waxy rice starch at low $T_g - T_a$ under the thermodynamic control whereas the opposite result was found when it was under kinetic control. This difference between the two starches was due to their

Table 1
The maximum of ΔH_∞ and minimum of peak range (T_r) for $T_g - T_a$

Sample	ΔH_∞		T_r	
	Maximum ΔH_∞ (J/g)	$T_g - T_a$ (°C)	Minimum T_r (°C)	$T_g - T_a$ (°C)
NRS11	1.645	31.4	12.6	31.9
NRS13	2.390	20.2	10.0	31.9
NRS15	3.299	19.6	7.3	24.6
WRS11	1.865	29.1	14.9	27.7
WRS13	2.314	23.4	11.2	25.9
WRS15	2.894	14.4	10.3	16.0

different T_g's. The higher T_g of normal starch resulted in a shift of the plot to the higher $T_g - T_a$ range.

The intersection from two lines corresponding to thermodynamic and kinetic control was referred to as the maximum ΔH_∞. The maximum ΔH_∞ and the corresponding $T_g - T_a$ value were measured, and given in Table 1. The maximum ΔH_∞ increased with moisture content for both normal and waxy rice starches. This was from the restricted molecular mobility by reduced free volume as the moisture content was lowered. For a cross-linked epoxy resin (Cook et al., 1999), the relaxation enthalpy was less than that of the counterpart, because of the molecular restriction required for aging. The maximum ΔH_∞ is dependent on the ΔC_p as described in Eqs. (1) and (2). The ΔC_p increase by raising moisture content resulted in an increase of the maximum ΔH_∞ (Table 1). Normal rice starch had higher maximum ΔH_∞ values than did waxy rice starch, which could be also explained by the higher ΔC_p for normal rice starch.

The $T_g - T_a$ value for the maximum ΔH_∞ decreased as the moisture content increased, and was higher for normal than for waxy rice starch (Table 1). This value was found to be 10 ~ 15 °C for poly(ethylene terephthalate) (Aref-Azar et al., 1996) and 15 ~ 20 °C for epoxy resin (Cook et al., 1999). Our experimental result was relatively higher than those values.

The overall results suggest that the enthalpy relaxation of the amorphous normal and waxy rice starches was found to be highly dependent on the residual moisture content. The difference between aging and glass temperatures ($T_g - T_a$) was an important and theoretical variable to determine ΔH_∞ for relaxation. When a starch is stored at the temperature for maximum ΔH_∞, the greatest change in mechanical and physical properties could be expected, theoretically with trends in increasing storage modulus and density, and decreasing the volume and molecular mobility. Thus, the storage stability of glassy starch products could be minimized.

3.5. Peak range of enthalpy relaxation

The temperature range (T_r) for enthalpy relaxation endotherm in DSC thermogram is shown in Fig. 8. The overall curves had the shape reversed to that for ΔH_∞ (Fig. 7). It implies that the relaxation peak becomes narrower, when the enthalpy increases. Like the case for ΔH_∞, the temperature range changes according to $T_g - T_a$ was also explainable by the two different control mechanisms: thermodynamic ($T_g - T_a < 20 \sim 30$ °C) and kinetic controls ($T_g - T_a > 20 \sim 30$ °C). Under the thermodynamic control, the slope ($dT_r/dT_g - T_a$) was similar for both normal and waxy rice starches, although the temperature range (T_r) was slightly higher for normal rice starch. Again this was caused by a higher T_g for normal rice starch. However, under kinetic control, the slope was much greater for normal rice starch. In this range ($T_g - T_a > 45$ °C), the transition temperature range for normal starch was wider than that of waxy starch, whereas the opposite result was shown when the temperature was closer to thermodynamic control (20 °C $< T_g - T_a <$ 45 °C). When the sample was aged at a temperature substantially higher than T_g ($T_g - T_a > 45$ °C), the segmental mobility became more restricted and the relaxation peak was separated from the glass transition. In that system, the heterogeneous structure with amylose and amylopectin in normal rice starch might cause a broadening of the enthalpy relaxation peak. However, the molecular mobility increased as the $T_g - T_a$ was raised. This raised mobility may easily modify the aging behavior of the linear amylose chain. The aging behavior of amylose may cause their peak range to become narrower. Further studies should be carried out in order to find the clear and detailed effects of amylose and amylopecin.

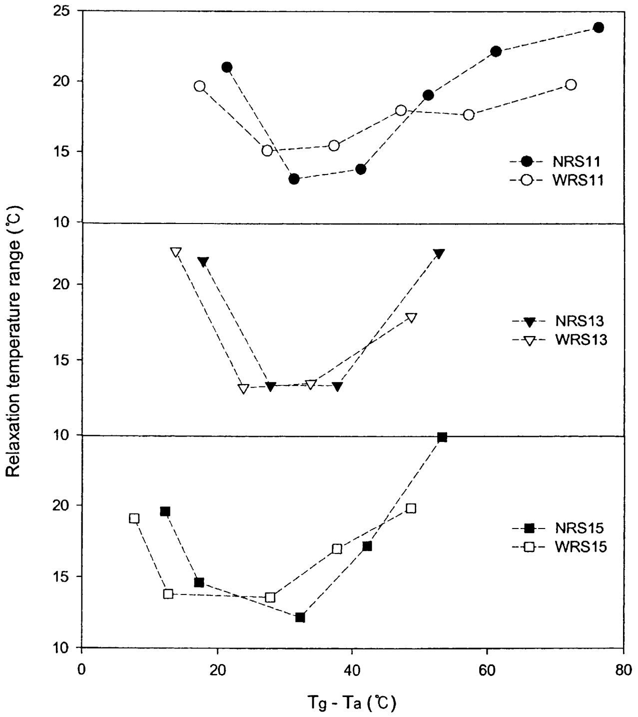

Fig. 8. The peak range of enthalpy relaxation versus $T_g - T_a$ of normal and waxy rice starches.

The minimum T_r and the corresponding $T_g - T_a$ were determined by intersecting both lines under the kinetic and thermodynamic controls in a similar way to that for the maximum ΔH_∞ (Table 1). The minimum T_r decreased with moisture content, and it was also smaller for normal rice starch because of the effect of the presence of the linear amylose chain as previously discussed. The $T_g - T_a$ at minimum T_r also increased as moisture content decreased, and was higher for normal rice starch. This result was similar to the $T_g - T_a$ results for maximum ΔH_∞ indicating that the relaxation occurred with the greatest change in physical properties such as enthalpy, volume, and density. As with ΔH_∞, the observation of minimum T_r for enthalpy relaxation peak could be another useful tool for predict storage-induced physical changes of glassy starch products.

4. Conclusions

The glass transition temperature (T_g) decreased but the heat capacity increment (ΔC_p) at T_g increased as the aging temperature (T_a) approached the glass transition temperature. This observation indicates that the mobility of the amorphous chain segments is substantially raised when T_a approaches T_g.

The maximum enthalpy relaxation (ΔH_∞) was not linearly correlated with $T_g - T_a$, because the system was controlled both kinetic and thermodynamic controls that depended on $T_g - T_a$. At a low $T_g - T_a$, the relaxation enthalpy (ΔH_∞) approached a thermodynamic limit due to nearly equilibrated structure, whereas at a high $T_g - T_a$, the relaxation was under kinetic control because the relaxation rate was positively related to the aging temperature. The slope ($\mathrm{d}\Delta H_\infty/\mathrm{d}T_g - T_a$) increased with moisture content, suggesting that the segmental mobility becomes more restricted due to insufficient moisture.

When ΔH_∞ was maximum, the peak range (T_r) became minimum. The $T_g - T_a$ for the maximum ΔH_∞ or minimum T_r reduced as the residual moisture content increased. Normal and waxy rice starches exhibited slightly different values for ΔH_∞ and T_r at a same $T_g - T_a$, although their changes by $T_g - T_a$ were similar. But the presence of amylose in starch resulted in structural heterogeneity influencing the physical aging characteristics of the starch. The ΔH_∞ relations to $T_g - T_a$ could be useful for optimizing storage temperature for starch-based glassy products by minimizing the physical changes occurring on.

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