Recrystallization Kinetics and Glass Transition of Rice Starch Gel System

Moo-Yeol Baik, Kwang-Joong Kim,* Ki-Cheol Cheon, Yeon-Chul Ha, and Wang-Soo Kim

Food Division, Agency for Defense Development, P.O. Box 35-1, Yuseong, Taejon, 305-600, Korea

The effect of storage temperature on recrystallization and glass transition temperature (T_g) of nonwaxy and waxy rice starch gel systems containing 60% moisture content was investigated by differential scanning calorimetry to understand the relationship between them. The nucleation and propagation for the recrystallization process were determined by recrystallization degree obtained from crystallite melting enthalpy changes during storage. The recrystallization rate for both rice starch gels within 3 days of storage and its temperature dependence were analyzed by Avrami and Arrhenius equations. The maximum nucleation and propagation for recrystallization of both rice starch gel systems occurred at 4 °C and 30 °C, respectively. The T_g slightly increased with increasing recrystallization degree, and the highest T_g was observed in the maximum recrystallization temperature ranges. The T_g and recrystallization rate of nonwaxy rice starch gel were changed more than those of the waxy one, while the higher activation energy and Q_{10} value were shown in waxy rice starch gel.

INTRODUCTION

Starch is a partially crystalline polymer which has amorphous, intercrystalline, and crystalline regions (Slade and Levine, 1987; Biliaderis, 1992); thus, it should exhibit two phase transitions when heated in water. One is the melting transition of the crystalline region, and the other is the glass transition of the amorphous region (Maurice et al., 1985; Biliaderis et al., 1986). Donovan (1979) was the first to work on the phase transition of starch; most of the phase transition studies mainly using differential scanning calorimetry (DSC), in the past focused on the first-order melting transition of the crystalline phase of starch.

However, since Slade and co-workers (Slade, 1984; Maurice et al., 1985) recognized the existence of a second-order transition (glass transition), many studies have been reported on the glass transition temperature (T_g) of starch–water systems and starch blends using DSC (Maurice et al., 1985; Biliaderis et al., 1986; Slade and Levine, 1988, 1989), dynamic mechanical thermal analysis (DMTA) and NMR (Kalichevsky et al., 1992, 1993), and permeability (Arvanitoyannis et al., 1994, 1996).

The gelatinized starch has no crystallites, which means that the crystalline region of starch changes into an amorphous region. If the gelatinized starch is stored, nonequilibrium recrystallization depends on storage conditions such as time, temperature, and moisture content, and the starch becomes retrograded (Levine and Slade, 1989). The retrogradation of starch has been defined as "a process which occurs when the molecules comprising gelatinized starch begin to reassociate in an ordered structure" (Atwell et al., 1988).

The Avrami theory has been widely applied to determining the retrogradation rate of starch gels and cooked rice (McIver et al., 1968; Colwell et al., 1969; Kim et al., 1976, 1996; Kim and Kim, 1984), and recently some

other equations, such as the Williams–Ferry–Landel (WLF) equation and the Hoffman equation, were used to study the kinetics of the crystallization process (van Krevelen, 1990; Arvanitoyannis and Blanshard, 1994).

In many starchy foods, the recrystallization and the glass transition of starch play key roles in the quality and storage stability of the products. Therefore, the control of these processes is very important for keeping the quality of starch-containing food products (Ablett et al., 1986; Levine and Slade, 1989; Ward et al., 1994).

The degree of recrystallization and the nature of the recrystallites formed may be affected by starch source, storage temperature, concentration, and the presense of salts, acids, lipids, surfactants, and sugars (Orford et al., 1987; Zeleznak and Hoseney, 1986; Slade and Levine, 1987; Eliasson and Ljunger, 1988; Russell and Oliver, 1989).

It was also found that the glass transition temperature (T_g) is specific for each compound and depends on the free volume, degree of polymerization, molecular geometry, crystallinity, and average molecular weight of the polymer (Levine and Slade, 1988, 1989; Slade and Levine, 1989, 1991). The T_g of starch is sensitive to the amount of diluent present (Biliaderis, 1991). Low molecular weight diluent such as water or plasticizer depresses the T_g of a polymer (starch)–water system (Levine and Slade, 1988, 1989; Biliaderis, 1991).

Although many recent studies have been reported on the recrystallization and glass transition of starch–water systems, there are few reports on the relationship between recrystallization and glass transition. In this study, we investigated the recrystallization and the glass transition of nonwaxy and waxy rice starch gel systems containing 60% moisture content as a function of storage temperature by DSC to find out their relationship.

MATERIALS AND METHODS

Source of Rices. Dongjin rice, as a nonwaxy rice starch source, and sinsun waxy rice, as a waxy rice starch source,

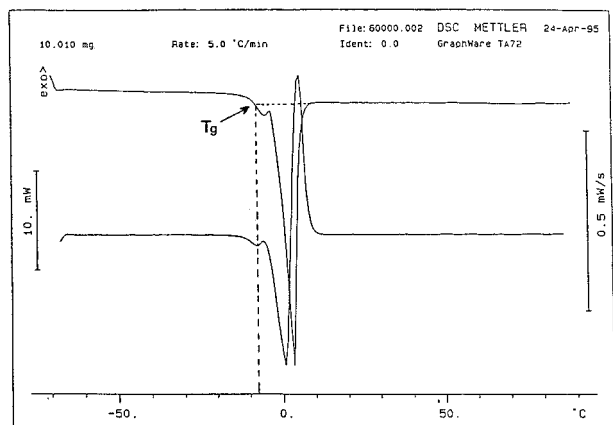* Author to whom correspondence should be addressed [tel 82-42-821-4683; fax 82-42-821-2391].

Recrystallization Kinetics and Glass Transition of Rice

J. Agric. Food Chem., Vol. 45, No. 11, 1997 **4243**

Figure 1. DSC thermogram of T_g for a high-moisture rice starch gel system.

were obtained from Rural Development Administration, Suwon, Korea. Dongjin rice contains about 20% amylose, and sinsun waxy rice contains a little amylose content. Both rices were the first season's crop of 1994.

Isolation of Rice Starch. The rice was soaked in deionized water for 8 h and ground in two volumes of 0.2% (w/v) NaOH solution with a Waring blender for 3 min. The rice suspension was passed through a 100-mesh sieve and allowed to stand at 4 °C for 24 h. The supernatant was removed, and two volumes of 0.2% (w/v) NaOH solution were added under stirring, and then the solution was kept at 4 °C for 24 h. This process was repeated until the protein was completely removed. The resulting sediment was washed with deionized water until neutral pH was achieved. The isolated starch was dried to a moisture content of 12% at 25 °C and ground to pass through a 100-mesh sieve. All starch samples were stored at 4 °C.

Thermal Analysis by DSC. For rice starch gel preparation, about 10 mg of each rice starch suspension was prepared by adding deionized water to the above starch samples to achieve 60% (w/w) of moisture content. The suspensions were sealed in coated aluminum DSC crucibles with aluminum stoppers (Mettler ME-27331). The sample pans were heated from 20 to 100 °C in a differential scanning calorimeter (Mettler TA-4000 system, DSC 30U.K.) at a heating rate of 5 °C/min. An empty pan was used as the reference. Subsequently, the gelatinized samples were stored at various temperatures to allow them to recrystallize, during which time the effect of storage temperature on recrystallization was observed.

To find out the recrystallization kinetics of rice starch gels, two different experiments were conducted. First, in order to determine the effect of temperature on nucleation, rice starch gels with 60% moisture content were stored at −20, −12, 0, 4, 20, 30, 40, 50, and 60 °C, respectively. Second, for the determination of the effect of temperature on propagation, rice starch gels with 60% moisture content were stored at 4 °C for 2 days to nucleate, and then these samples were put into incubation chambers set at 30, 40, 50, and 60 °C, respectively. After storage, the samples were reheated as mentioned above. Melting temperatures and crystallite melting enthalpies were measured from DSC thermograms, and the degree of recrystallization was calculated as the percentage of the enthalpy at time t over the gelatinization enthalpy.

To investigate the T_g, gelatinized and stored samples were cooled at the maximum rate (about 40 °C/min) to −70 °C, and then reheated to 100 °C at a heating rate of 5 °C/min.

The T_g of rice starch gel was determined from the DSC thermogram using the first derivative curve of heat flow to time (Figure 1).

Analysis of Recrystallization Rate and Its Temperature Dependence. The recrystallization rate was analyzed by the Avrami equation (Colwell et al., 1969).

$$\theta = \frac{E_L - E_t}{E_L - E_0} = \exp(-kt^n) \tag{1}$$

$$\log\left(-\ln\frac{E_L - E_t}{E_L - E_0}\right) = \log k + n \log t \tag{2}$$

where θ is the noncrystallization part at time t, E_0 is the enthalpy at time 0, E_t is the enthalpy at time t, E_L is the maximum enthalpy, k is the rate constant (time^{-1}), and n is the Avrami exponent.

The influence of temperature on starch recrystallization rate is represented by Q_{10},

$$Q_{10} = (\text{recryst. rate at } T + 10/\text{recryst. rate at } T) \tag{3}$$

where T is the absolute temperature (K).

The temperature dependence of the recrystallization rate was analyzed by the Arrhenius equation (Labuza, 1982),

$$k = A \exp^{-E_a/RT} \tag{4}$$

$$\ln k = \ln A - E_a/RT \tag{5}$$

where A is the Arrhenius constant, E_a is the activation energy (cal/mol), R is a constant (1.987 cal/(mol K), T is the absolute temperature (K), and k is the rate constant (time^{-1}).

The relationship between Q_{10} and activation energy (E_a) was analyzed by the following equation (Labuza, 1982):

$$\log Q_{10} = \frac{2.19 \, E_a}{(T) \, (T + 10)} \tag{6}$$

where E_a is the activation energy and T is the absolute temperature (K).

RESULTS AND DISCUSSION

Effect of Temperature on Recrystallization. The changes in degree of recrystallization of nonwaxy and waxy rice starch gels during storage at various temperatures are shown in Figure 2. The maximum recrystallization of both rice starch gels at a single storage temperature occurred at 4 °C, and the degree of recrystallization leveled off after 9 days of storage, whereas very little or no recrystallization was found below −20 and above 30 °C.

The increase of recrystallization degree during storage at a single temperature can be considered as a nucleation step for recrystallization. It has been reported that recrystallization at single temperature was observed between T_g and the crystallite's melting temperature (T_m), and the maximum nucleation occurs just above T_g (Slade and Levine, 1988). However, our results provide information on the specific temperature range for recrystallization (nucleation) of rice starch gel, in which the maximum nucleation occurred well above 0 °C, that is, refrigeration temperature range, and the recrystallization was found to occur in rice starch gel at temperatures below T_g.

In contrast to the nucleation of rice starch gel, the degree of recrystallization of rice starch gels after nucleation at 4 °C for 2 days, which means propagation occurred, is shown in Figure 3. The recrystallization of rice starch gel already possessing the nuclei occurred up to 50 °C, and the maximum propagation was observed at 30 °C. This temperature range is a little lower than the T_m of rice starch, which is somewhat different from the results for semicrystalline synthetic polymers and for B-type starch (Slade and Levine, 1988). This result indicates that the nuclei formed at
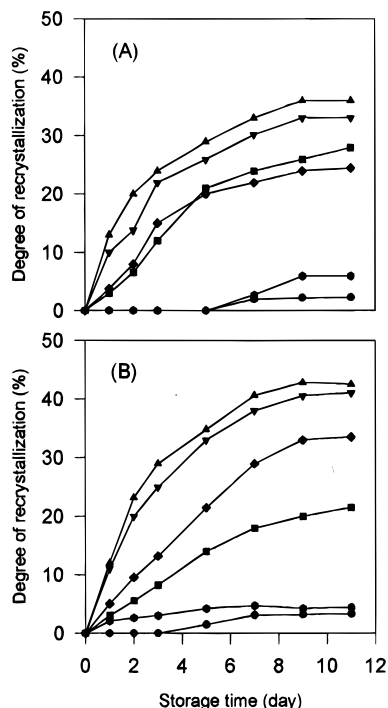
4244 *J. Agric. Food Chem.,* Vol. 45, No. 11, 1997

Baik et al.

Figure 2. Changes in degree of recrystallization of nonwaxy (A) and waxy (B) rice starch gels during storage at various temperatures; ●, 30; ■, 20; ▲, 4; ▼, 0; ◆, −12; ◗, −20 °C.
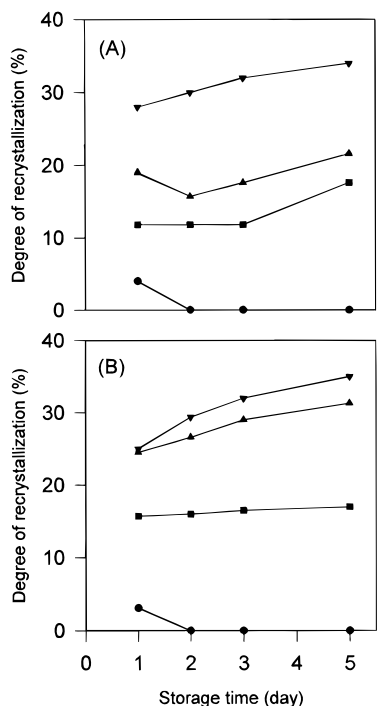

Figure 3. Changes in degree of recrystallization of nonwaxy (A) and waxy (B) rice starch gels during storage at various temperatures, after nucleation at 4 °C for 2 days; ●, 60; ■, 50; ▲, 40; ▼, 30 °C.

4 °C for 2 days might be melted at temperatures above 30 °C, and the melting degree increased with increasing storage temperature due to the instability. These results are similar to those reported, showing that the greatest rate and extent of staling in the shortest time are achieved by faster nucleation at 0 °C for long enough to allow extensive nucleation, followed by faster propagation at 40 °C (Slade, 1984; Zeleznak and Hoseney, 1987).
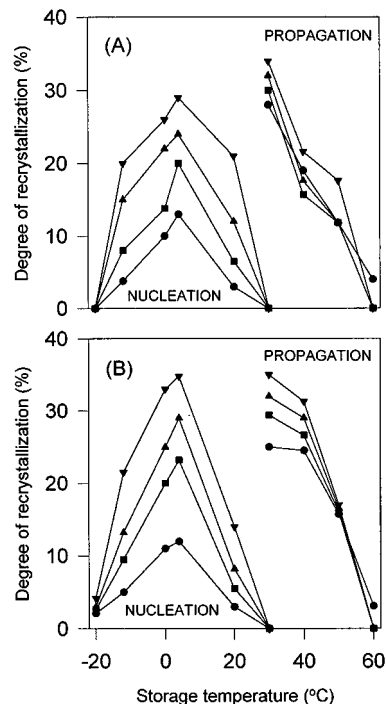

Figure 4. Recrystallization kinetics of nonwaxy (A) and waxy (B) rice starch gels containing 60% moisture, expressed in terms of the degree of recrystallization as a function of temperature: ●, 1 day; ■, 2 days; ▲, 3 days; and ▼, 5 days.
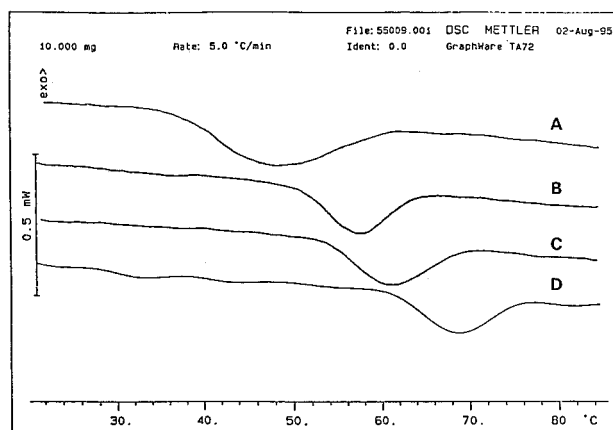

Figure 5. Crystallite melting endotherm of rice starch gel stored at different temperatures and times, (A) 4 °C for 5 days; (B) 4 °C for 2 days, then 30 °C for 3 days; (C) 4 °C for 2 days, then 40 °C for 3 days; (D) 4 °C for 2 days, then 50 °C for 3 days.

Figure 4 shows the recrystallization kinetics of both rice starch gels containing 60% moisture, expressed in terms of the degree of recrystallization as a function of temperature. The maximum nucleation and propagation occurred near 4 and at 30 °C, respectively. However, it could be assumed that the maximum degree of overall recrystallization for rice starch gel at a single temperature still occurs near the maximum nucleation temperature. This fact has been noted as a clear indication that the recrystallization process for B-type starch is strongly nucleation-limited (Slade and Levine, 1988).

The crystallite's melting endotherm of nucleation was observed in the range from 35 to 61 °C, but in propagation it shifted to higher temperature with respect to storage temperature, resulting in stopping near the gelatinization temperature (Figure 5). It seems that the crystallites grown at high temperatures are more stable
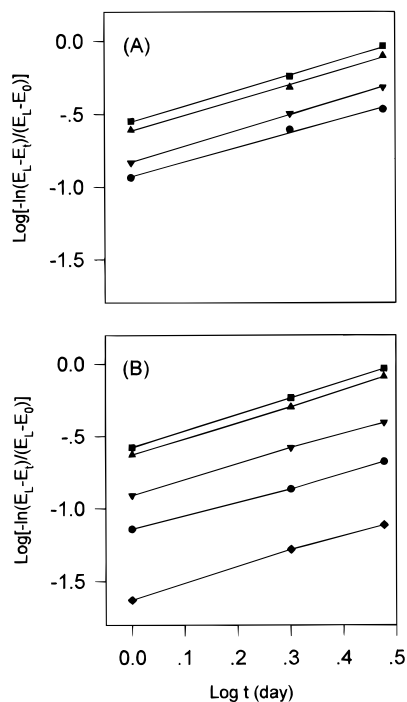
Recrystallization Kinetics and Glass Transition of Rice

J. Agric. Food Chem., Vol. 45, No. 11, 1997 **4245**

Figure 6. Plot of $\log[-\ln(E_L - E_t)/(E_L - E_0)]$ against log time of nonwaxy (A) and waxy (B) rice starch gels stored at various temperatures: ●, 20; ■, 4; ▲, 0; ▼, −12; and ◆, −20 °C.

Figure 7. Plot of $\ln(E_L - E_t)$ against time of nonwaxy (A) and waxy (B) rice starch gels stored at various temperatures: ●, 20; ■, 4; ▲, 0; ▼, −12; and ◆, −20 °C.

and closer to the shape and size of crystallites of native starch. These results also can be explained on the basis that the recrystallization of rice starch gel is very sensitive to storage temperature at a constant moisture content, which may be governed by the interaction between molecules of crystallite, leading to changes in the shape of the crystallite.

Recrystallization Rate and Its Temperature Dependence. Data on the effect of temperature on the recrystallization kinetics of rice starch gel suggested that the overall process is nucleation controlled; thus, the changes of recrystallization degree within 3 days of storage, which has an exponentially linear relationship with time, can be analyzed by the Avrami equation (Figure 6). The 35% and 41% recrystallization degrees, which were the values after 9 days of storage at 4 °C for nonwaxy and waxy rice starch gels, respectively, were used as the maximum degrees of recrystallization (E_L). The Avrami exponents (n) of both rice starch gels obtained by plotting $\log[-\ln\{(E_L - E_t)/(E_L - E_0)\}]$ against $\log t$ were close to 1.0. This fact indicates that recrystallization of rice starch gel during 3 days of storage at a single temperature has instantaneous nucleation, followed by rodlike growth of crystals (McIver et al., 1968).

When the Avrami exponent is equal to 1.0, the rate constant (k) was determined from the graph of $\ln(E_L - E_t)$ versus time (Figure 7). Avrami exponents (n) and time constants ($1/k$, reciprocal rate constants) for both rice starch gels at various storage temperatures are listed in Table 1. The values of time constants for both rice starch gels were found to be lowest at 4 °C and increased at the other storage temperature ranges. This result agrees with the trends in the change of recrystallization degree.

However, the recrystallization rate of waxy rice starch was slower than that of the nonwaxy one, which is the reverse of the phenomenon observed in the change of recrystallization degree. According to the work of Miles et al. (1985), Ring et al. (1987), and Gidley and co-
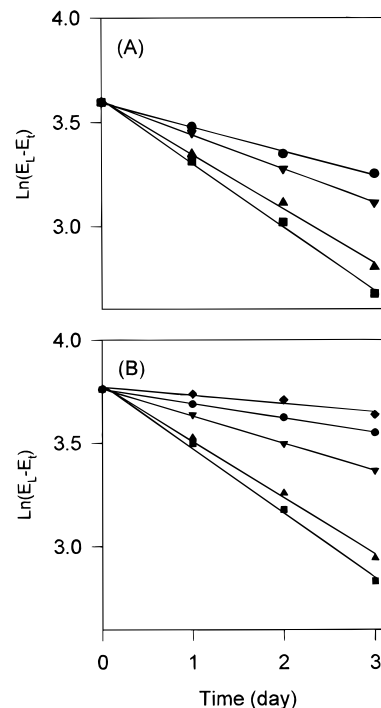
workers (Clark et al., 1989; Gidley, 1989), starch retrogradation occurs at two kinetically distinct process: (1) rapid gelation of amylose via formation of double-helical chain segments, followed by helix−helix aggregation, and (2) slow recrystallization of the short amylopectin chains. Thus, the above result might be because the reaction rate in the initial stage of recrystallization is dependent on the amylose content of rice starch.

The temperature dependence of the recrystallization rate analyzed by the Arrhenius equation was plotted (Figure 8). It has been reported that the temperature dependence of reaction rates in the rubbery state ($T_g < T < T_g + 100$ °C) does not obey the typical Arrhenius response (Levine and Slade, 1986). But our data on recrystallization kinetics for both nonwaxy and waxy rice starch gels within 3 days of storage well followed the Arrhenius relation. This is illustrated by the time-dependent development of the storage modulus of amylose and amylopectin gels (Biliaderis, 1992).

The activation energy (E_a) was determined from the slope of the Arrhenius plot, and the Q_{10} value was calculated from eq 6 (Table 2). It was reported that the activation energy was −4.47 kcal/mol and the Q_{10} value was 1.26 at room temperature in the retrogradation of cooked rice (Kim et al., 1996). Meanwhile, in the case of bread retrogradation, the activation energy and Q_{10} value were −8.84 and 1.67 kcal/mol, respectively (Labuza, 1982). The activation energy and Q_{10} value of waxy rice starch gels were higher than those of the nonwaxy one, but these values were between those of cooked rice and bread. On the other hand, the activation energies and Q_{10} values of both rice starch gels were changed at 4 °C. Higher activation energy and Q_{10} value were observed above than below 4 °C, indicating that the change of the recrystallization rate below 4 °C is smaller than that above 4 °C. This result is similar to the report by Huang et al. (1994) that wheat starch

Table 1. Avrami Exponents (*n*) and Time Constants (1/*k*, Days) of Rice Starch Gels Containing 60% Moisture Content during Storage at Various Temperatures

	storage temp									
	−20 °C		−12 °C		0 °C		4 °C		20 °C	
	n	1/*k*	*n*	1/*k*	*n*	1/*k*	*n*	1/*k*	*n*	1/*k*
nonwaxy			1.08	6.173	1.05	3.817	1.09	2.865	0.99	8.621
waxy	1.09	25.126	1.06	7.559	1.05	3.210	1.05	3.188	1.01	13.643
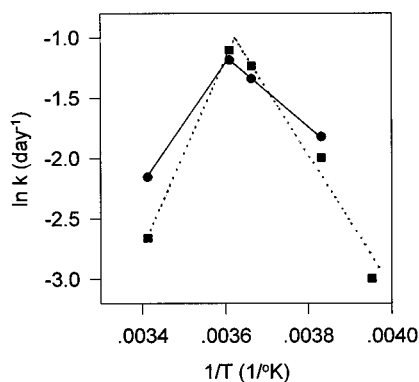
Figure 8. Arrhenius plot for the recrystallization rate of nonwaxy and waxy rice starch gels stored at various temperatures for 3 days: ●, nonwaxy rice starch gel; ■, waxy rice starch gel.

Table 2. Activation Energies (*E*ₐ) and *Q*₁₀ Values of Rice Starch Gels Containing 60% Moisture Content during Storage at Various Temperatures

	temp ranges (°C)			
	below 4 °C		above 4 °C	
	E_a (cal/mol)	Q_{10}	E_a (cal/mol)	Q_{10}
nonwaxy	2.87×10^3	1.22	-4.92×10^3	1.34
waxy	5.99×10^3	1.52	-7.89×10^3	1.62

gels, rice flours, and rice starch gels have smaller enthalpy below zero than above zero by DSC.

Changes of T_gs during Recrystallization. The changes of T_gs for both nonwaxy and waxy rice starch gels containing 60% moisture content stored at various temperatures were shown in Figure 9. The T_gs of gelatinized nonwaxy and waxy rice starch were −7.8 and −7.2 °C, respectively. It has been observed that a glass transition appears at −7 °C in retrograded gels with 55% total moisture content (Slade and Levine, 1984).

There were progressive increase in the T_gs of both rice starch gels stored at 20, 4, 0, and −12 °C with increasing storage time, and a significant increase of T_gs was observed in the range of 0−4 °C.

This result demonstrates that there is a good correlation between the nucleation degree for recrystallization and T_g of the rice starch gel system, and the change of T_g for rice starch gel stored at a single temperature is also nucleation limited. Huang et al. (1994) also observed that the T_g of rice starch gel increased progressively during the storage and that the extent of the increase was affected by the storage temperature. Evidences from semicrystalline synthetic polymers and starches show that, as the degree of crystallinity increases, the T_g also increases (Jin et al., 1984; Zeleznak and Hoseney, 1987; Levine and Slade, 1989; Roos and Karel, 1991). The recrystallization caused by reassociation of starch molecules with hydrogen bonding might decrease the amount of effective plasticizing water and increase the T_g (Biliaderis, 1992). Consequently, as the ratio of crystalline to amorphous regions is increased, T_g should be increased.
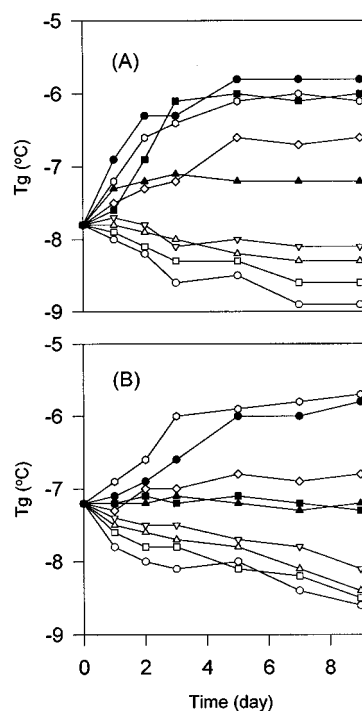
Figure 9. Changes of T_gs for nonwaxy (A) and waxy (B) rice starch gels containing 60% moisture content during storage at various temperatures: ○, 60; □, 50; △, 40; ▽, 30; ◇, 20; ⊘, 4; ●, 0; ■, −12; and ▲, −20 °C.

On the other hand, the T_g of nonwaxy rice starch gel was changed greater than that of the waxy one upon storage at all storage temperatures, which is closely connected with the difference of the recrystallization degrees between two rice starch gels. Presumably, this is because of the amylose content of nonwaxy rice starch, which could lead to the amorphous region rather than the crystalline region.

The decrease of the T_gs of both rice starch gels stored above temperatures in the 30 °C range, in which propagation occurred well, was observed. This might be explained by the exothermic peak, T_d, following the glass transition attributed to the crystallization of unfrozen water (Figure 10). During the rapid decrease in temperature, the water in gel stored at a high temperature did not freeze and was maintained in a glassy state during the cooling treatment on the gelatinized sample. When the sample was reheated from −70 to 100 °C for the T_g determination, the devitrification occurred. The T_d was then detected following T_g by the crystallization of the devitrified water (Simatos et al., 1975; Liu and Lelievere, 1992; Huang et al., 1994). Huang et al. (1994) also observed the occurence of this T_d peak during reheating of rice starch and rice flour gels. On the other hand, when the samples were stored in the range from −12 to 20 °C (recrystallization progressed), T_d disappeared due to the decrease of the plasticizable water in the amorphous region during recrystallization. Thus, at high temperatures, the formation of T_d might be attributed to the decrease of T_g.
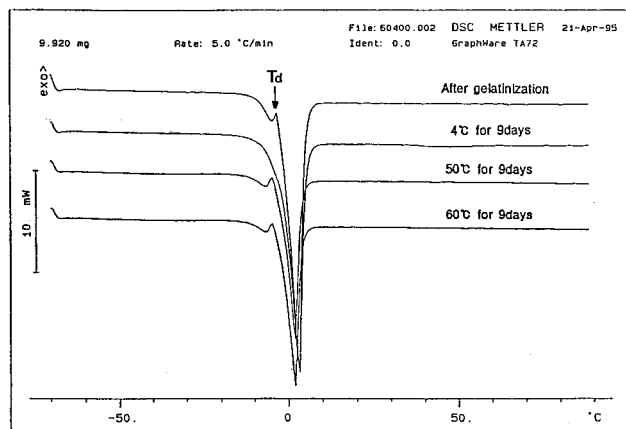
Recrystallization Kinetics and Glass Transition of Rice

J. Agric. Food Chem., Vol. 45, No. 11, 1997 **4247**

Figure 10. Ice melting endotherm for high-moisture rice gels stored at different temperatures.
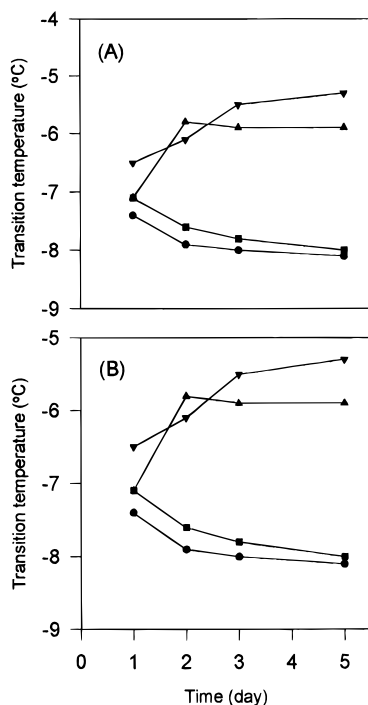

Figure 11. Changes of T_gs for nonwaxy (A) and waxy (B) rice starch gels during storage at various temperatures, after nucleation at 4 °C for 2 days: ●, 60; ■, 50; ▲, 40; and ▼, 30 °C.

Figure 12. Kinetically expressed T_gs of nonwaxy (A) and waxy (B) rice starch gels containing 60% moisture stored at various temperatures: ●, nucleated for 5 days; ■, nucleated at 4 °C for 2 days, then propagated for 3 days.

The changes of T_gs for both nonwaxy and waxy rice starch gels prenucleated at 4 °C for 2 days are shown in Figure 11. The T_g gradually increased in the range of 30−40 °C, showing the greatest increase at 30 °C, and there were a little changes of T_gs above 50 °C in both rice starch gel systems. The results from the changes of T_gs in the rice starch gel system confirmed that increasing the degree of recrystallization resulted in increasing T_g.

The changes of T_gs of both rice starch gels during storage at various temperatures are shown in Figure 12. The change of T_g was relatively high in the range of 0−4 °C for the nucleation step and at 30 °C for the propagation step, corresponding with the results of the kinetics of recrystallization.

Conclusions. Trends of the recrystallization for nonwaxy and waxy rice starch gels during storage were similar, but the degree of recrystallization was greater in the waxy one. The maximum nucleation occurred at 4 °C, and the maximum propagation was observed at
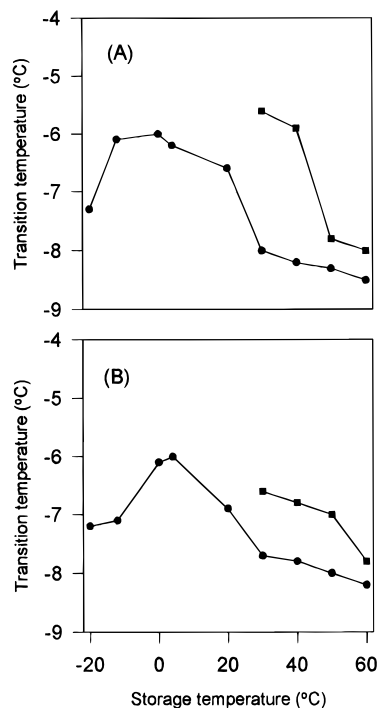
30 °C in both rice starch gels. The crystallite melting endotherm was shown in the range of 35−61 °C, but, in propagation, it shifted to higher temperatures. The time constants for waxy rice starch gel, calculated from the Avrami equation, were greater than those for nonwaxy one, whereas the recrystallization rate of waxy rice starch gel was slower than that of the nonwaxy one. The data on the recrystallization rates of both rice starch gels during 3 days of storage well followed the Arrhenius relation, and E_a and Q_{10} values were between those of cooked rice and bread. The maximum change of T_g for both rice starch gels was also observed in the range of 0−4 °C during nucleation and at 30 °C during propagation. The change of the T_g of nonwaxy rice starch gel was greater than that of the waxy one. The results from T_g changes showed that there is a good relationship between glass transition and recrystallization in the rice starch gel system.

LITERATURE CITED

Ablett, S.; Attenburrow, G. E.; Lillford, P. J. The significance of water in the baking process. In *Chemistry and Physics of Baking*; Blanshard, J. M. V., Frazier, P. J., Galliard, T., Eds.; Royal Society of Chemistry: London, U.K., 1986; pp 30−41.

Arvanitoyannis, I.; Blanshard, J. M. V. Rates of crystallization of dried lactose-sucrose mixtures. *J. Food Sci.* **1994**, *59* (1), 197−205.

Arvanitoyannis, I.; Kalichevsky, M. T.; Blanshard, J. M. V.; Psomiadou, E. Study of diffusion permeation of gases in undrawn and uniaxially drawn films made from potato and rice starch conditioned at different relative humidities. *Carbohydr. Polym.* **1994**, *24*, 1−15.

Arvanitoyannis, I.; Psomiadou, E.; Nakayama, A. Edible films made from sodium caseinate, starches, sugars or glycerol. *Carbohydr. Polym.* **1996**, *31*, 179−192.

Atwell, W. A.; Hood, L. F.; Varriano-Marston, E.; Zobel, H. F. The terminology and methodology associated with basic starch phenomena. *Cereal Foods World* **1988**, *33*, 306−311.

Biliaderis, C. G. Non-equilibrium phase transitions of aqueous starch systems. In *Water Relationships in Foods*; Levine,

4248 *J. Agric. Food Chem.,* Vol. 45, No. 11, 1997

Baik et al.

H., Slade, L., Eds.; Plenum Publishing: New York, 1991; pp 251−273.

Biliaderis, C. G. Structures and phase transition of starch in food systems. *Food Technol. (Chicago)* **1992**, *46* (6), 98−109.

Biliaderis, C. G.; Tonogai, J. R. Influence of lipids on the thermal and mechanical properties of concentrated starch gels. *J. Agric. Food Chem.* **1991**, *39*, 833−840.

Biliaderis, C. G.; Page, C. M.; Maurice, T. J.; Juliano, B. O. Thermal characterization of rice starches: A polymeric approach to phase transitions of granular starch. *J. Agric. Food Chem.* **1986**, *34*, 6−14.

Clark, A. H.; Gidley, M. J.; Richarderson, P. K.; Ross-Murphy, S. B. Rheological studies of aqueous amylose gels: The effects of chain length and concentration on gel modulus. *Macromolecules* **1989**, *22*, 346−351.

Colwell, K. H.; Axford, D. W. E.; Chamberlain, N.; Elton, G. A. H. Effect of storage temperature on the aging of concentrated wheat starch gels. *J. Sci. Food Agric.* **1969**, *20*, 550−555.

Donovan, J. W. Phase transitions of starch-water system. *Biopolymers* **1979**, *18*, 263−275.

Eliasson, A. C.; Ljunger, G. Interaction between amylopectin and lipid additives during retrogradation in a model system. *J. Sci. Food Agric.* **1988**, *44*, 353−361.

Gidley, M. J. Molecular mechanisms underlying amylose aggregation and gelation. *Macromolecules* **1989**, *22*, 351−358.

Huang, R. M.; Chang, W. H.; Chang, Y. H.; Lii, C. Y. Phase transition of rice starch and flour gels. *Cereal Chem.* **1994**, *71* (2), 202−207.

Jin, X.; Ellis, T. S.; Karasz, F. E. The effect of crystallinity and cross linking on the depression of the glass transition temperature in the nylon 6 by water. *J. Polym. Sci.: Polym. Phys. Ed.* **1984**, *22*, 1701−1717.

Kalichevsky, M. T.; Blanshard J. M. V. A study of the effect of water on the glass transition of 1:1 mixtures of amylopectin, casein, and gluten using DSC and DMTA. *Carbohydr. Polym.* **1992**, *19*, 271−278.

Kalichevsky, M. T.; Blanshard J. M. V. The effect of fructose and water on the glass transition of amylopectin. *Carbohydr. Polym.* **1993**, *20*, 107−113.

Kalichevsky, M. T.; Jaroszkiewicz, E. M.; Ablett S.; Blanshard J. M. V.; Lillford, P. J. The glass transition of amylopectin measured by DSC, DMTA and NMR. *Carbohydr. Polym.* **1992**, *18*, 77−88.

Kalichevsky, M. T.; Jaroszkiewicz, E. M.; Ablett S.; Blanshard J. M. V. A study of the glass transition of amylopectin-sugar mixtures. *Polymer* **1993**, *34*, 346−358.

Kim, I. H.; Kim, S. K. Effects of phosphates differing in P_2O_5 contents on firming rate of cooked rice. *Cereal Chem.* **1984**, *61* (2), 91−94.

Kim, S. K.; Ciacco, C. F.; D'Appolonia, B. L. Kinetic study of retrogradation of cassava starch gels. *J. Food Sci.* **1976**, *41*, 1249−1250.

Kim, S. K.; Lee, A. R.; Lee, S. K.; Kim, K. J.; Chun, K. C. Firming rates of cooked rice differing in moisture content. *Korean J. Food Sci.* **1996**, *28* (5), 877−881.

Labuza, T. P. *Shelf-life Dating of Foods*; Food & Nutr. Press, Inc.: Westport, CT, 1982; Chapter 12.

Levine, H.; Slade, L. A polymer physico-chemical approach to the study of commercial starch hydrolysis products (SHPs). *Carbohydr. Polym.* **1986**, *6*, 213−244.

Levine, H.; Slade, L. Water as a plasticizer: Physico-chemical aspects of low-moisture polymeric systems. In *Water Science Reviews*; Franks, F., Ed.; Cambridge University Press: Cambridge, 1988; Vol. 3, pp 79−185.

Levine, H.; Slade, L. Influence of the glassy and rubbery state of the thermal, mechanical, and structural properties of doughs and baked products, In *Dough Rheology and Baked Product Texture, Theory and Practice*; Faridi, H., Faubino, J. M., Eds.; van Nostrand Reinhold AVI: New York, 1989; pp 157−330.

Liu, H.; Lelievre, J. Transitions in frozen gelatinized starch systems studied by differential scanning calorimetry. *Carbohydr. Polym.* **1992**, *17*, 145−149.

Maurice, T. J.; Slade, L.; Sirett, R. R.; Page, C. M. Polysaccharide-water interaction: Thermal behavior of rice starch. In *Properties of Water in Foods*; Simatos, D., Multon, J. L., Eds.; Martinus Nijhoff Publishers: Dortrecht, The Netherlands, 1985; pp 211−227.

McIver, R. G.; Axford, D. W. E.; Cowell, K. H.; Elton, G. A. H. Kinetic study of the retrogradation of gelatinized starch. *J. Sci. Food Agric.* **1968**, *19*, 560−563.

Miles, M. J.; Morris, V. J.; Orford, P. D.; Ring, S. G. Roles of amylose and amylopectin in gelation and retrogradation of starch. *Carbohydr. Res.* **1985**, *135*, 271−281.

Orford, P. D.; Ring, S. G.; Carroll, V.; Milles, M. J.; Morris, V. J. The effect of concentration and botanical source on the gelation and retrogradation of starch. *J. Sci. Food Agric.* **1987**, *39*, 169−177.

Ring, S. G.; Collona, P.; L'Anson, K. J.; Kalichevsky, M. T.; Miles, M. J.; Orford, P. D. The gelation and crystallization of amylopectin. *Carbohydr. Res.* **1987**, *162*, 277−293.

Roos, Y.; Karel, M. Plasticizing effect of water on thermal behavior and crystallization of amorphous food models. *J. Food Sci.* **1991**, *56*, 38−43.

Russel, P. L.; Oliver, G. The effect of pH and NaCl content on starch gel ageing. A study by differential scanning calorimetry and rheology. *J. Cereal Sci.* **1989**, *10*, 123−138.

Simatos, D.; Faure, M.; Bonjour, E.; Couach, M. Differential thermal analysis and differential scanning calorimetry in the study of water in foods. In *Water Relations in Foods*; Duckworth, R. B., Ed.; Academic Press: New York, 1975.

Slade, L. Starch Properties in processed foods: staling of starch-based products. *Abstracts of Papers*, 69th Annual Meeting of AACC, Minneapolis, MN; AACC: ST. Paul, MN, 1984; Abstr. 112.

Slade, L.; Levine, H. Recent Advances in Starch Retrogradation. *Recent Developments in Industrial Polysaccharides*; Gordon and Breach Sci.: New York, 1987.

Slade, L.; Levine, H. Thermal Analysis of Starch, *Abstracts of Papers,* 1988 CRA Scientific Conference; Corn Refiners Assoc.: Washington, DC, 1988; pp 169−244.

Slade, L.; Levine, H. A food polymer science and retrogradation. In *Frontiers in Carbohydrate Research-1: Food Applications*; Millane, R. P., BeMiller, J. N., Eds.; Elsevier Applied Science: New York, 1989; pp 215−270.

Slade, L.; Levine, H. *CRC Crit. Rev. Food Sci. Nutr.* **1991**, *30*, 115−360.

van Krevelen, X. *Properties of Polymers*, 3rd ed.; Elsevier: Amsterdam, 1990; pp 585−623.

Ward, K. E. J.; Hoseney, R. C.; Seib, P. A. Retrogradation of Amylopectin from maize and wheat starches. *Cereal Chem.* **1994**, *71* (2), 150−155.

Zeleznak, K. J.; Hoseney, R. C. The role of water in the retrogradation of wheat starch gels and bread crumbs. *Cereal Chem.* **1986**, *63* (5), 407−411.

Zeleznak, K. J.; Hoseney, R. C. Characterization of starch from bread aged at different temperature. *Starch* **1987**, *39*, 231−233.