

Changes in Retrogradation Properties of Rice Starches with Amylose Content and Molecular Properties

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ABSTRACT

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The increases in storage modulus (G'), retrogradation enthalpy change (ΔH) and ΔH -related Avrami kinetic parameters of gelatinized rice starch dispersions at 25% (w/w) were investigated with respect to storage period, amylose content (AC), and molecular properties. Three high-AC and five low-AC rice cultivars were compared for understanding the multiple influences of AC and molecular properties involved. After refining the results of correlation analysis, the G' of just-cooled samples changed positively, mainly with AC and additionally with the average chain length of amylose (CL_{AM}) and the weight ratio of extra-long plus

long chains to short chains of amylopectin (AP) ($r_{APchain}$). The developed ΔH on short-term storage (10 days) elevated with increasing AC and CL_{AM} and decreasing degree of polymerization of AP (DP_{AP}), but after long-term aging for one to three months with increasing $r_{APchain}$, especially for the low-AC cultivars examined. Greater Avrami rate constants for retrogradation could be attributed to the combination of a lower DP_{AP} and $r_{APchain}$ or AP chain length and a greater CL_{AM} . The polynomials using these critical factors to describe the retrogradation parameters were elucidated and could account for 85–99.6% of data deviations.

Retrogradation of gelatinized starch materials involves formation and subsequent aggregation of double helices of amylose (AM) and amylopectin (AP) chains (van Soest et al 1994) governing elasticity, firmness, and textural staling of starch-containing systems (Atwell et al 1988). Basically, AM retrogradation occurs on cooling and very short-term aging (Doublier and Choplin 1989; Biliaderis and Zawistowski 1990; Silverio et al 1996), while AP retrogradation proceeds slowly during aging and requires several weeks or months of storage for equilibrium (Miles et al 1985; Biliaderis and Zawistowski 1990; Lai et al 2000). Amylose content (AC) bestows critical influences on the elastic property of freshly retrograded starch dispersions (Radhika Reddy et al 1994; Lii et al 1996) and on the hardness of freshly cooked rice (Roferos and Juliano 1997; Champagne et al 1999; Bett-Garber et al 2001). And AP tend to have additional effects on the extent of retrogradation of starches (Yuan et al 1993) or on the hardness of short-term staled cooked rice through the proportion of extra-long and long-B chains (Radhika Reddy et al 1993; Ramesh et al 1999; Lai et al 2001).

Nonetheless, for some rice cultivars with similar AC, the increases in elasticity of starch gels or in staling of cooked rices (Roferos and Juliano 1997; Champagne et al 1999) remain unexpected solely in terms of the proportion of extra-long and long-B chains in AP. This uncertainty is especially noteworthy when rice starch systems like sterilized cooked rice and rice cakes experience long-term storage before being consumed. Therefore, interpreting the elastic changes and AP-induced staling of starch gels during long-term storage are quite essential and requires consideration of more molecular effects and of kinetic viewpoints. There are indications that the Avrami kinetic parameters for retrogradation of starch materials vary with AP properties (Mua and Jackson 1997, 1998; Lai et al 2000), with AC in starch (Zhang and Jackson 1992; Mua and Jackson 1998), and potentially with nonstarch compositions in rice flour (Fan and Marks 1998; Teo et al 2000). However, few studies have been done to clarify these changes in retrogradation parameters for rice starches as a function of multiple starch factors.

This study investigated the changes in short- and long-term retrogradation properties of gelatinized rice starch dispersions as a function of AC and representative molecular properties. Storage

moduli (G') and retrogradation enthalpy changes (ΔH) were examined as an index for short- and long-term retrogradation behaviors, respectively, where ΔH data were further employed to derive the Avrami kinetic parameters of retrogradation. Three high-AC and five low-AC rice cultivars were compared; some possess similar AC but with obviously different retrogradation tendencies. For example, IR 24 vs. Sinandomeng, Taichung 189 (TC189) vs. Taichung Sen 10 (TCS10), and Kaoshiung Sen 7 (KSS7) vs. Taichung native 1 (TCN1) and Taichung Sen 17 (TCS17). The AC and molecular properties in AM or AP have been reported elsewhere (Tseng 1995; Lu et al 1997; Huang et al 1998, 1999; Lai et al 2000, 2001).

MATERIALS AND METHODS

Rice Cultivars

IR24 and Sinandomeng rice were harvested in the Philippine dry season of 1997. KSS7, TC189, TCN1, TCS10, and Tainung 67 (TNU67) rice were harvested in the second crop season of Taiwan 1998. All rice starches were isolated and purified with an alkaline steeping method (Yang et al 1984). The apparent amylose contents (AC) are reported as 11.3 wt% for IR24, 10.7 wt% for Sinandomeng (Lai et al 2001), 25.9 wt% for KSS7, 14.3 wt% for TC189, 16.5 wt% for TNU67, 27.6 wt% for TCN1, and 15.6 wt% for TCS10 (Lii et al 1998). Some retrogradation properties of KSS7 and TCS17 (AC 26.1 wt%) rice starches have been reported (Lin et al 2001) and were not examined again. Sinandomeng, TC189, and TNU67 are japonica cultivars and the others are indica cultivars (Lai and Lii 2000; Boisen et al 2001). According to the classification of Juliano (1982), KSS7, TCN1, and TCS17 starches are high-AC cultivars (AC >25 wt%) and the others are low-AC cultivars (AC 10–20 wt%).

Dynamic Rheological Measurements

A controlled stress rheometer (Carri-Med CSL-100, TA Instruments Ltd., Surrey, England) was used to perform oscillatory shear experiments using parallel plate geometry (20 mm diameter and 1,000 μm gap). Starch dispersions at 25 wt% in water were preheated with gentle stirring in a water bath at 70°C for 1 min to minimize settling out of starch granules, followed by careful pouring into circular stainless steel molds (80 mm i.d. \times 1 mm depth) without trapping any visible bubbles. The molds were sealed and heated in a boiling water bath for 30 min for complete gelatinization of starch dispersions, cooled rapidly to 4°C, and then aged for 0–7 days. Before rheological measurements, the pasty or gelled samples in the molds were allowed to equilibrate at room temper-

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ature for 1 hr and loaded onto the peltier of the rheometer thermostat at 25°C, where the gelled samples were cut into disks 20 mm in diameter and loaded very carefully to avoid mechanical damage. A layer of light silicone oil was applied to the exposed edge of sample to eliminate dehydration. Storage moduli (G') of starch gels were recorded under a strain of 4% and a frequency of 1.0 Hz, where the strain was determined from preliminary experiments and within the viscoelastic linearity for the pasty, weak gels of the low-AC samples. Aging periods of the detected samples were no longer than seven days because low G' deviations were readily obtained, especially for high-AC rice starches under the stain applied. Data are means of three replicate measurements.

DSC Analysis

A portion of 25 wt% starch suspension (≈ 120 mg, containing 0.02% NaN_3) equilibrated at room temperature for 1 hr was hermetically sealed in a stainless steel crucible with a stainless steel stopper and aluminum O-ring. The sealed crucible was heated in an air-oven at 130°C for 1 hr, followed by cooling and aging at 4°C for 0–80 days. The retrograded samples were heated from 10 to 130°C at 5°C/min in a Setaram DSC 121 system (Caluire Cedex, France). An empty sealed crucible was used as reference. The enthalpy changes (ΔH , J/g of dry starch) for melting of starch crystallites formed during retrogradation were measured in three replicates.

Calculation of Retrogradation Kinetics

According to the kinetic treatments of Fan and Marks (1998) and Lai et al (2000), the increase in enthalpy change (ΔH) during starch retrogradation can be described with the Avrami equation (Eq. 1) (Avrami 1940; Wunderlich 1997) and alternatively expressed as Eq. 2.

$$\theta = (\Delta H_\infty - \Delta H_t) / (\Delta H_\infty - \Delta H_0) = \exp(-k t^n) \quad (1)$$

$$\log(-\ln \theta) = n \log t + \log k \quad (2)$$

where θ is the fraction of crystallization resting to take place; ΔH_0 and ΔH_t are the ΔH (J/g starch) at storage times of 0 and t days, respectively; ΔH_∞ is the limiting ΔH at infinite times ($t \rightarrow \infty$) and obtained from the intercept of $1/\Delta H_t$ vs. $1/t$ plot; n and k are the Avrami exponent and rate constant (per day) derived from the slope and intercept of $\log(-\ln \theta)$ vs. $\log t$ plot.

Statistical Analysis

Pearson's correlation and multiple regression procedures were performed with v. 6.12 software for Windows (SAS Institute, Cary, NC). Avrami kinetic parameters were obtained by using SigmaPlot 8.0 software (SPSS Institute, Chicago, IL) by least-squared fits.

RESULTS AND DISCUSSION

Rheological Properties and Retrogradation

Figure 1 shows the storage moduli (G') developments of the rice starches examined at 25 wt% during short-term storage. The G' values of the KSS7 starch gels increased significantly at the first day of storage; while those of TCN1 increased after the second day of storage and more progressively than the KSS7. In low-AC cultivars, the G' values increased slightly during the first five days but remarkably thereafter in the order of TC189 > IR24 \approx TNU67 \geq TCS10 \geq Sinandomeng at day 7.

Considering the observed G' values with respect to AC and the preparation condition applied, the AC dependencies of G'_0 (G' at the beginning of storage) of the rice starch dispersions prepared in a hermetic stainless mold are depicted in Fig. 2 (filled circles), in comparison with the reported samples freely gelatinized on the peltier of a dynamic rheometer (open circles) (Lii et al 1995). In the front systems, the logarithmic G'_0 of low-AC samples linearly depended on AC with a comparable slope (0.039) but lower intercept by ≈ 0.8 than the freely gelatinized samples of AC 1–26%.

However, both high-AC cultivars (KSS7 and TCN1) prepared in a hermetic mold closely followed the AC-dependence of the freely gelatinized systems. This possibly relates to the granular integrity that can partially explain the G'_0 changes of starch cooks on cooling (Svegmarm et al 1993; Lii et al 1996) because low-AC rice starches are prone to granular disintegration during gelatinization (Tester and Morrison 1990; Radhika Reddy et al 1994; Lii et al 1995; Chen et al 2003).

Recrystallization Properties and Kinetics

For the rice starches detected, the enthalpy changes (ΔH) for melting of microcrystallites formed during long-term storage were observable at 35–64°C by DSC and mainly concern chain organization of AP (Miles et al 1985; Biliaderis and Juliano 1993). Figure 3A indicates that the increasing rate of ΔH was most drastic for KSS7, followed by TCN1. Both samples showed a rapidly increasing profile between the first four days and ≈ 20 days of storage, respectively. Comparably, the ΔH values of the low-AC rice starches were detectable after the first 10 days of storage and maximized for at least 70 days. Among low-AC cultivars, the ΔH started to differ after one month of storage and finally became greatest for IR24 and TCS10 and least for TNU67. In the Avrami kinetics (Fig. 3B), obvious two-stage and one-stage linearities were discovered for the high-AC and low-AC starches, respectively. The critical days for separating different slopes were used to identify early- and late-stage retrogradation periods of the front systems (KSS7 and TCN1).

Table I shows that the infinite enthalpy changes (ΔH_∞) of 25 wt% rice starches during retrogradation were 5.6–8.4 J/g, estimated from the tendency of the averaged ΔH data at infinite time. The reduced ΔH_∞ ($\Delta H_{\infty,R}$) ranged from 6.7 to 11.3 J/g, where $\Delta H_{\infty,R} = \Delta H_\infty / (1 - \text{AC}\%)$ because the ΔH data are AP-related (Miles et al

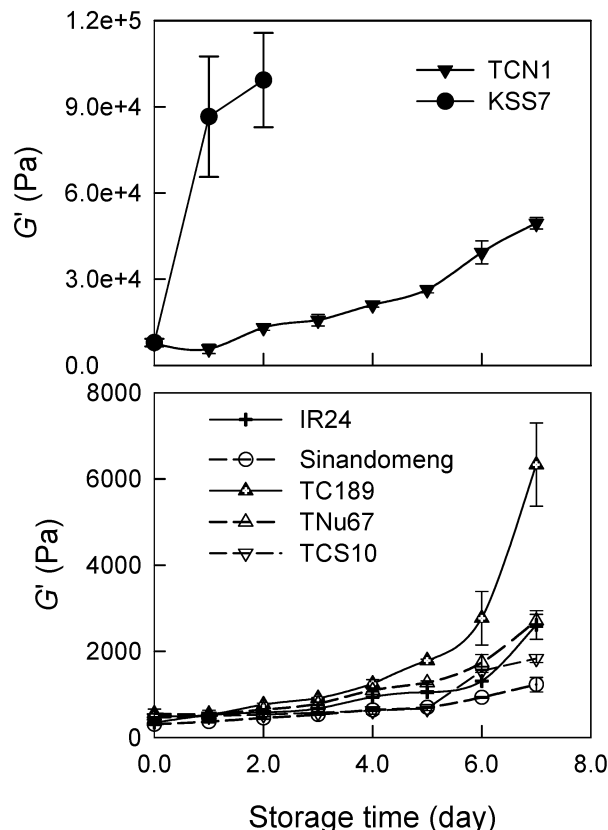


Fig. 1. Increases in storage modulus (G') of gelatinized starch dispersions with storage time t (samples gelatinized in stainless steel molds, starch concentration 25 wt%, storage at 4°C).

1985; Biliaderis and Juliano 1993). The high-AC samples showed a greater Avrami exponent (n_I) and lower rate constant (k_I) for early-stage storage ($n_I = 1.02\text{--}1.63$, $k_I = 4.2 \times 10^{-1} \text{--} 6.5 \times 10^{-2} \text{ day}^{-n}$) than those for late-stage storage ($n_{II} = 0.34\text{--}0.70$, $k_{II} = 1.0\text{--}2.5 \times 10^{-1} \text{ day}^{-n}$). The n_{II} and k_{II} parameters were apparently

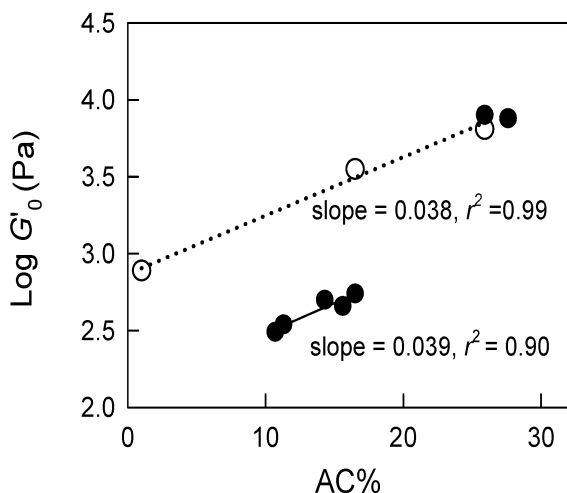


Fig. 2. Changes in logarithmic G'_0 (0 storage time) of gelatinized rice starch dispersions with apparent amylose content (AC) in this study (●) (starch concentration 25 wt%). Data for samples freely gelatinized on the peltier of dynamic rheometer are compared (○ [Lii et al 1995]).

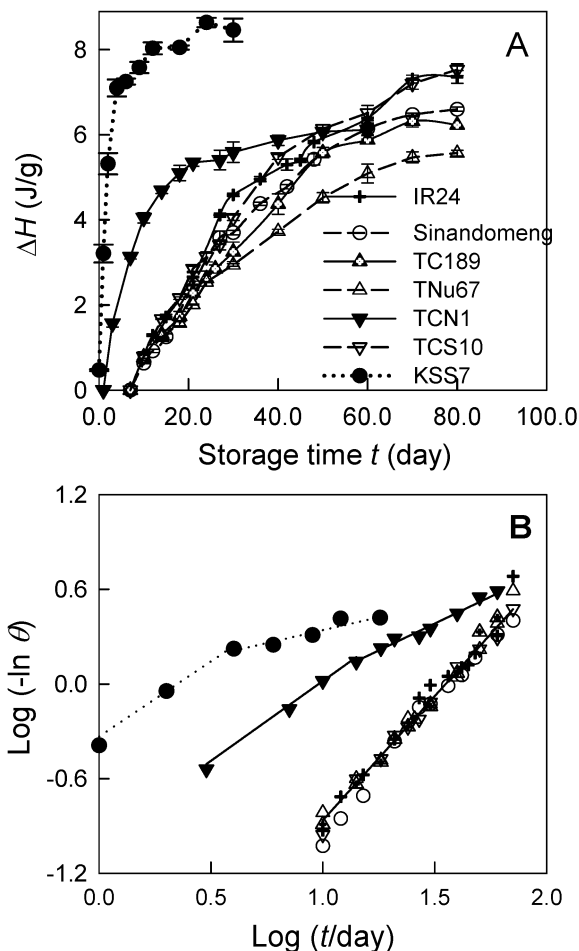


Fig. 3. Increases in retrogradation enthalpy change (ΔH) with storage time (A) and Avrami plots (B) of gelatinized starch dispersions. Starch concentration 25 wt%, $\theta = (\Delta H_\infty - \Delta H_t)/(\Delta H_\infty - \Delta H_0)$ for 0, t , and ∞ days of storage time.

less and more, respectively, than those of low-AC starches ($n_{II} = 1.51\text{--}1.76$, $k_{II} = 2.1 \times 10^{-3} \text{--} 4.7 \times 10^{-3} \text{ day}^{-n}$). All kinetic parameters accounted for $\geq 91\%$ of data deviations (R^2 0.91–1.00). Similar tendencies in n and k with AC exist for flours of four American rice cultivars at 28.6 wt% (Fan and Marks 1998).

Generally, a higher n value accompanied a lower k value for starch retrogradation, as in isolated AP (Lai et al 2000) and other rice flour systems (Fan and Marks 1998). Figure 4 further indicates the relationship between the logarithmic k and n values for the high-AC rice starches during early- and late-stage storage. They commonly followed the linearity of the rice AP overall storage (solid line, slope -1.01 , $r^2 = 0.915$) (Lai et al 2000). However, the data of the low-AC cultivars were below the linearity, resulting in another excellent linearity for late-stage retrogradation of all rice starches (dotted line, slope -1.89 , $r^2 = 0.996$). In comparison, the Avrami constants for 28.6 wt% rice starch of AC = 28.4 wt%, some American rice flours (AC 15.1–25.6 wt%) (Fan and Marks 1998) and those for the rice flour and starch of Makmur 77 cultivars (AC ≈ 21 wt%) at 33.3 wt% (Teo et al 2000) are slightly above the linearity of the rice AP. The effects of nonstarch compositions in flour on reducing k (Teo et al 2000) are comparably insignificant. The significantly low k of low-AC cultivars agrees with the low G'_0 (Fig. 2).

Significance of AC and Molecular Properties

To facilitate understanding, some molecular properties of the rice starches reported elsewhere (Tseng 1996; Lu et al 1997; Huang et al 1998; Lai et al 2001) that showed significant correlations with the retrogradation parameters are tabulated (Table II). The number-average degree of polymerization (DP_n), chain length (CL), exterior CL (ECL), interior CL (ICL), and the weight ratio of extra-long chain plus long chain to short chain ($r_{APchain}$) of the rice AP examined are, respectively, in the range of 1,743–10,470 gu, 15.3–22.1 gu, 10.8–15.8 gu, 3.2–5.3 gu, and 0.54–0.71 in average. The CL of whole amylose fractions (CL_{AM}) and the DP_n of the low molecular weight subfractions ($F_2\text{--}DP_n$) are 202–430 gu and 343–441 gu, respectively.

Table III indicates the significant correlation coefficients between the retrogradation parameters and molecular properties of all rice starches examined, where the ΔH at day 10 of storage (ΔH_{10}) was used as an index of short-term (10–30 days) AP-related retrogradation. The G' at the day 0 of storage (G'_0) correlated positively with AC, the CL, ECL, ICL, and $r_{APchain}$ of AP, and the CL of AM

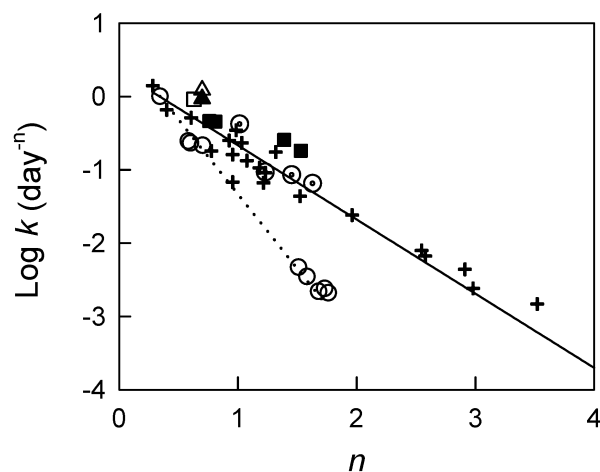


Fig. 4. Relationships between Avrami rate constant (k) and exponent (n) for early-stage (●) and late-stage (○) retrogradation of gelatinized rice starches at 25 wt%. Experimental conditions and kinetic parameters are defined in Table I. Reported data incorporated for comparison: rice amylopectins at 60 wt% (solid line [Lai et al 2000]), rice starches (□, △), and rice flours (■, ▲) at 28.6 wt% (■, □ [Fan and Marks 1998]) and 33.3 wt% (▲, △ [Teo et al 2000]).

(CL_{AM}), and negatively with the DP_n of AP (DP_{AP}). But the G' at day 7 of storage (G'_7) of the samples, excluding undetectable KSS7, became closely related with both AC and $r_{APchain}$, more than with the other molecular parameters. The ΔH_{10} and $\Delta H_{\infty,R}$ showed similar but less significant correlations than did the G'_0 . No significant correlations were found for ΔH_{∞} . The k_1 , which existed only for the high-AC rice starches examined, correlated closely and negatively with all DP_n, CL, ECL, and ICL of AP and potentially positively with the F_2 -DP_n of AM. The significant correlation coefficients for n_{II} were contrary to those for G'_0 . A greater k_{II} occurred with a lower DP_{AP} and greater CL_{AM}.

Nonetheless, high-AC rice starches in general have AP with a lower DP_n, but greater CL, ECL, and ICL, as well as proportion of extra-long plus long chains (greater $r_{APchain}$) (Takeda et al 1987; Hizukuri et al 1989; Radhika Reddy et al 1993; Lu et al 1997) and have AM with a greater upper limit in DP_n distribution (Huang et al 1998). These molecular properties are ambiguously interactive on starch retrogradation. The real roles of AC as well as AP and AM properties need to be refined to describe changes in the retrogradation parameters. By excluding the data of high-AC samples, significant correlation coefficients between the properties of low-AC cultivars (AC 11–17%) (Table IV) suggest that G'_0 significantly correlated only with AC and with CL_{AM} potentially. The ΔH_{∞} and $\Delta H_{\infty,R}$ increased significantly and potentially, respectively, only with increasing $r_{APchain}$. The correlation coefficients for all starches (Table III) did not appear anymore. Accordingly, the significance of AC and CL_{AM} on G'_0 and of $r_{APchain}$ on ΔH for low-AC rice starches would hold for all rice starches as well, and were primarily considered for certain retrogradation parameters.

Interpretation of Retrogradation Properties

Table V lists empirical equations for the examined retrogradation parameters for all rice starches, except further indications, in terms of the significant factors concluded from Tables III and IV. The functions tabulated were those with greatest multiple correlation coefficients (R^2). The equation with $10^{0.039AC}$, where the exponent was from that $\log G' \propto 0.039AC$ (Fig. 2), CL_{AM} and $r_{APchain}$ could describe 97.5% of G'_0 deviations ($R^2 = 0.975$). A similar explainable percentage in G'_0 deviation was also achieved by the equation with AC⁴ instead of $10^{0.039AC}$, because $G' \propto AC^{3.8}$ and AC^{4.2}, respectively, are for defatted rice starches with high and low gelatinization temperatures (GT) (Biliaderis and Juliano 1993). The equations with AC, CL_{AM}, and DP_{AP} for ΔH_{10} , with $r_{APchain}$ for ΔH_{∞} (for the low-AC cultivars only) and with AC and $r_{APchain}$ for $\Delta H_{\infty,R}$ accounted for ≈ 85 – 92% of the ΔH variations ($R^2 = 0.854$ – 0.917).

The k_1 of high-AC rice starches could be very satisfactorily expressed with a function of DP_{AP} and the chain length of AP (CL_{AP}) ($R^2 = 0.996$). A function of DP_{AP}, CL_{AM}, and $r_{APchain}$ explained $\approx 89\%$ of k_{II} deviations. While 92% of n_{II} changes depended on the same factors for G'_0 . The roles of these significant factors (AC, CL_{AM}, DP_{AP}, $r_{APchain}$, and CL_{AP}) agree with the concept that starch retrogradation involves successive association processes of AM chains mainly on cooling (Doublier and Choplin 1989; van Soest et al 1994; Silverio et al 1996) and AP chains on aging, of which extra-long and long-B chains organize after initial aging (Lai et al 2001) and more rapidly than short chains (DP_n \leq 15 gu) (Miles et al 1985; Doublier and Choplin 1989; Keetels et al 1996; Silverio et al 1996).

TABLE I
Enthalpy Changes and Avrami Kinetics Parameters for Retrogradation of 25 wt% Rice Starches at 4°C^a

Cultivars	ΔH_{∞}^b (J/g)	$\Delta H_{\infty,R}^b$ (J/g)	Early Stage			Late Stage		
			n_I	k_I	R^{2c}	n_{II}	k_{II}	R^2
TCN1	6.3	8.6	1.23	9.3×10^{-2}	0.98	0.70	2.2×10^{-1}	0.97
TCN1 ^d	7.0	9.7	1.63	6.5×10^{-2}	0.96	0.60	2.3×10^{-1}	0.98
TCS17 ^d	7.0	9.5	1.45	8.5×10^{-2}	0.95	0.58	2.5×10^{-1}	0.99
KSS7 ^d	8.4	11.3	1.02	4.2×10^{-1}	1.00	0.34	1.0	0.91
TNu67	5.6	6.7	nd ^e	nd	nd	1.51	4.7×10^{-3}	0.99
TCS10	7.6	9.0	nd	nd	nd	1.58	3.5×10^{-3}	0.99
TC189	6.3	7.4	nd	nd	nd	1.76	2.1×10^{-3}	0.98
IR24	7.4	8.3	nd	nd	nd	1.73	2.4×10^{-3}	0.97
Sinandomeng	6.6	7.4	nd	nd	nd	1.68	2.2×10^{-3}	0.99

^a Subscripts I and II for Avrami parameters (n and k are the Avrami exponent and rate constant day⁻ⁿ, respectively) represent early- and late-stage retrogradation, respectively. Data were mathematically derived from means of three replicates.

^b ΔH_{∞} , average infinite enthalpy changes of 25 wt% rice starches during prolonged storage, estimated from the intercept of $1/\Delta H_t - 1/t$ plot (t = storage time) mathematically derived from means of three replicates of raw data; $\Delta H_{\infty,R}$, reduced ΔH_{∞} [$= \Delta H_{\infty}/(1 - AC\%)$].

^c Multiple correlation coefficients by least-squared fits.

^d Kinetic data estimated from the original data of Lin et al (2001).

^e Not determined.

TABLE II
Molecular Properties of Rice Starches^a

Cultivars ^b	AP					AM	
	DP _n (gu)	CL (gu)	ECL (gu)	ICL (gu)	$r_{APchain}$	CL (gu)	$F_2 - DP_n$ (gu)
TCN1	2,827	22.1	15.8	5.3	0.71	335	378
TCS17	2,885	21.7	15.4	5.3	0.67	276	353
KSS7	1,743	20.2	14.5	4.7	0.65	430	436
TNu67	8,812	17.5	12.6	3.9	0.53	287	441
TCS10	6,481	18.8	13.4	4.3	0.57	249	343
TC189	10,470	15.4	11.3	3.2	0.54	333	373
IR24	5,276	17.2	12.0	4.2	0.56	202	nd ^c
Sinandomeng	8,706	15.3	10.8	3.5	0.56	214	nd

^a AP, amylopectin; AM, amylose; DP_n, number-average degree of polymerization; CL, average chain length; ECL, average exterior CL; ICL, average interior CL; $r_{APchain}$, average weight ratio of extra-long and long chains to short chains in AP; F_2 , low molecular weight subfraction of amylose fractions with a DP_n of 300–600 gu.

^b Data for IR24 and Sinandomeng cultivars are obtained from Lai et al (2001); other AP properties from Lu et al (1997). AM properties of KSS7 and TNu67 cultivars from Tseng (1996), other AM properties except for IR24 and Sinandomeng cultivars are from Huang et al (1998).

^c Not determined.

TABLE III
Significant Correlation Coefficients Between Physical Parameters for Retrogradation and Molecular Properties of Rice Starches

Property ^a	G'_0 ^b	G'_7 ^b	ΔH_{10} ^b	$\Delta H_{\infty,R}$	k_I	n_{II}	k_{II}
AC	0.95(7)*** ^c	0.93(6)**	0.89(9)***	0.69(9)*		-0.96(9)***	
AP							
DP _n	-0.85(7)*		-0.87(9)**	-0.86(9)**	-1.00(4)**	0.89(9)**	-0.68(9)*
CL	0.84(7)*	0.83(6)*	0.79(9)*	0.69(9)*	-0.98(4)*	-0.88(9)**	
ECL	0.85(7)*	0.84(6)*	0.80(9)*	0.69(9)*	-0.96(4)*	-0.89(9)**	
ICL	0.80(7)*		0.76(9)*	0.68(9)*	-1.00(4)**	-0.85(9)*	
$r_{APchain}$	0.93(7)**	0.96(6)**	0.83(9)**	0.69(9)*		-0.90(9)***	
AM							
CL	0.78(7)*		0.74(9)*			-0.70(9)*	0.79(9)*
$F_2 - DP_n$					0.93(4) ⁺		

^a AP, amylopectin; AM, amylose; DP_n, number-average degree of polymerization; CL, average chain length; ECL, average exterior CL; ICL, average interior CL; $r_{APchain}$, average weight ratio of extra-long and long chains to short chains in AP; F_2 , low molecular weight subfraction of amylose fractions with a DP_n of 300–600 gu.

^b G'_0 and G'_7 , G' values at 0 and after 7 days of storage, ΔH_{10} enthalpy at 10 days; k_I , n_{II} , and k_{II} are defined in Table I; starch concentration for retrogradation = 25 wt%. Subscripts I and II for Avrami parameters (n and k are the Avrami exponent and rate constant day⁻ⁿ, respectively) represent early- and late-stage retrogradation, respectively. ΔH_{∞} , average infinite enthalpy changes of 25 wt% rice starches during prolonged storage, estimated from the intercept of $1/\Delta H_t - 1/t$ plot (t = storage time) mathematically derived from means of three replicates of raw data; $\Delta H_{\infty,R}$, reduced ΔH_{∞} [= $\Delta H_{\infty}/(1 - AC\%)$].

^c +, *, **, and *** significant at $P = 0.07$, <0.05 , <0.01 , and <0.001 , respectively; numbers in parentheses are number of observations.

TABLE IV
Correlation Coefficients Between Physical Parameters for Retrogradation and Molecular Properties of Rice Starches with Low-Amylose Content (AC)

Property	Retrogradation		
	G'_0	ΔH_{∞}	$\Delta H_{\infty,R}$
AC	0.94(5)** ^b		
$r_{APchain}$		0.93(5)*	0.87(5) ⁺
CL _{AM}	0.85(5) ⁺		

^a AC, amylose content; CL_{AM}, chain length of whole AM; $r_{APchain}$, average weight ratio of extra-long and long chains to short chains in AP; ΔH_{∞} , average infinite enthalpy changes of 25 wt% rice starches during prolonged storage, estimated from the intercept of $1/\Delta H_t - 1/t$ plot (t = storage time) mathematically derived from means of three replicates of raw data; $\Delta H_{\infty,R}$, reduced ΔH_{∞} [= $\Delta H_{\infty}/(1 - AC\%)$]; G'_0 , G' at the beginning of storage;

^b + and * significant at $P = 0.06-0.07$ and <0.05 , respectively; number of observations in parentheses.

Accordingly, AC played a most significant role on G'_0 and short-term ΔH , as suggested from many reports on the G' of freshly cooled rice starch dispersions (Radhika Reddy et al 1994; Lii et al 1995, 1996; Tsai and Lii 2000) and the hardness of freshly cooked rice (Roferos and Juliano 1997; Lii et al 1998; Champagne et al 1999; Bett-Garber et al 2001). In addition, the rapid G' and ΔH increases and great ΔH_{∞} of KSS7 (Figs. 1 and 3, Table I), as compared with the other high-AC counterparts, could be attributed to the combination of comparably great CL_{AM} and low DP_{AP}. The greater G'_7 of TC189 than the other low-AC cultivars (Fig. 1) was most likely due to its greater CL_{AM} as well. In this study, the positive influences of CL_{AM} (in the range of 202–430 gu studied) on G' and k_{II} are different from those of synthetic AM, where CL >100 gu reduce crystallization tendency in solution by turbidity measurements (Gidley et al 1986). Variations in starch concentration and the physical indices may be responsible for such different CL effects. The molecular weights of AM on the ΔH of retrogradation in this study are not as important as for gels of corn starch AM (Mua and Jackson 1997).

In AP properties, the negative influences of DP_{AP} on k_I and k_{II} for rice starches (Tables III and V) concur with those on the initial retrogradation rate of wheat starches (Zhang and Jackson 1992) and the gel firmness of AP fractions from cornstarch (Mua and Jackson 1997). The positive roles of $r_{APchain}$ on the G'_0 and long-term ΔH of the rice starches agree with those of maize starches (Yuan et al 1993) strengthening the importance of extra-long and long B-chains in AP on staling of cooked rice (Radhika Reddy et al 1993; Ramesh et al 1999; Lai et al 2001). Short chains in AP may retard short-term retrogradation (Würsch and Gumy 1994;

Shi and Seib 1995) but co-crystallize with long chains to enhance retrogradation level on prolonged aging (Gidley and Bulpin 1987; Würsch and Gumy 1994). The latter possibility was implied by the negative correlation between k_{II} and $r_{APchain}$ (Tables III and V). Likely, moderate combinations of AP and AM properties are essential to control the desired degree of retrogradation of native starches.

KSS7 starch is also known to have high gelatinization temperatures (final GT 81–90°C), while the TCN1 and TCS17 are low-GT cultivars (conclusion GT 70–74°C) (Lii et al 1995; Lai and Lii 2000). Relating GT to molecular parameters suggests that a high-GT may relate to a greater CL_{AM} and lower DP_{AP} rather than CL_{AP}, which is reportedly important for some high-AC starches, excluding the AM property (Jane et al 1999; Wang et al 2002). These results also provide some possible explanation why intermediate- to high-GT rices exhibit a greater amylopectin-staling ability of cooked rice than do low-GT rice of similar AC cultivars (Perez et al 1993). But for low-AC cultivars, there were likely no correlations between GT and retrogradation tendencies during storage because IR24 and Sinandomeng possess a conclusion GT of $\approx 80^\circ\text{C}$ (Lai et al 2001) and the others are low-GT (conclusion GT 73–74°C) (Lii et al 1995; Lai and Lii 2000). The influences of AC and molecular properties on starch gelatinization remain to be investigated.

CONCLUSIONS

The complicated effects of critical factors including AC, CL_{AM}, $r_{APchain}$, DP_{AP}, and CL_{AP} on rice starch retrogradation have been identified to a greater extent, although AC and the molecular properties of rice starches are intrinsically interrelated. The G'_0 of gelatinized rice starches increased with the increments mainly in AC and additionally in CL_{AM} and $r_{APchain}$. Similar factors including DP_{AP} replacing $r_{APchain}$ were also suitable to describe ΔH increments on short-term retrogradation, exemplified with the ΔH at the first 10 days of storage. However, the final ΔH after storage of one to three months appeared to be determined by $r_{APchain}$ only, especially for the low-AC cultivars examined. Avrami rate constants for early- and late-stage retrogradation could be well explained with a function of DP_{AP} and some of CL_{AP}, $r_{APchain}$, or CL_{AM}, depending on the storage period. These results provide multiple viewpoints of describing complicated retrogradation behaviors of rice starches.

Moderate combinations of AC and molecular properties for controlling retrogradation and viscoelasticity of more diverse rice starches or for minimizing the staling of sterilized cooked rice during long-term storage are under investigation.

TABLE V
Estimated Equations for Retrogradation Parameters of Rice Starches^{a,b}

Parameter	Estimated Equation	R ²
G' ₀ (Pa)	= -2.06 × 10 ⁴ + 2.06 × 10 ^{4(0.039AC + 2)} + 13.8 CL _{AM} + 3.05 × 10 ⁴ r _{APchain} [-1.50 × 10 ⁴ + 6.06 × 10 ⁻³ AC + 12.2 CL _{AM} + 2.19 × 10 ⁴ r _{APchain}] ^c	0.975 0.977
ΔH ₁₀ (J/g)	= 0.282 + 5.60 × 10 ⁻² AC + 1.48 × 10 ⁻² CL _{AM} - 5.02 × 10 ⁻⁴ DP _{AP}	0.917
ΔH _∞ (J/g)	= -18.6 + 45.7 r _{APchain} (low AC rice starches)	0.874
ΔH _{∞,R} (J/g)	= -25.3 + 0.126 AC + 56.7 r _{APchain}	0.854
k _I	= 1.85 - 2.26 × 10 ⁻⁴ DP _{AP} - 5.15 × 10 ⁻² CL _{AP} (high AC rice starches)	0.996
k _{II}	= 1.72 - 1.01 × 10 ⁻⁴ DP _{AP} + 3.26 × 10 ⁻³ CL _{AM} - 3.16 r _{APchain}	0.888
n _{II}	= 3.63 - 5.47 × 10 ⁻² AC - 9.98 × 10 ⁻⁴ CL _{AM} - 1.81 r _{APchain}	0.921

^a AC, amylose content; AP, amylopectin; AM, amylose; CL_{AM}, chain length of whole AM; r_{APchain}, average weight ratio of extra-long and long chains to short chains in AP; ΔH₁₀, ΔH at the 10th day of storage; ΔH_∞, average infinite enthalpy changes of 25 wt% rice starches during prolonged storage, estimated from the intercept of 1/ΔH_t-1/t plot (t = storage time) mathematically derived from means of three replicates of raw data; ΔH_{∞,R}, reduced ΔH_∞ [= ΔH_∞/(1 - AC%)]; G'₀, G' at the beginning of storage; subscripts I and II for Avrami parameters (n and k are the Avrami exponent and rate constant day⁻ⁿ, respectively) represent early- and late-stage retrogradation, respectively; CL_{AM} and CL_{AP} (gu), average chain lengths of AM and AP fractions, respectively; DP_{AP} (gu), number-average degree of polymerization of AP.

^b Equations were obtained by least-squared methods on the data of all rice starches except further indications; R², multiple correlation coefficients.

^c Exponent for AC estimated from the results of Biliaderis and Juliano (1993) on defatted rice starches (G' ∝ ACⁿ, n = 3.8-4.2).

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