

CHENG-YI LIU^{1,2*}, VIVIAN M.-F. LAI³, SHIN LU⁴, MEI-LIN TSAI¹

CORRELATION BETWEEN THE PHYSICAL PROPERTY, EATING QUALITY AND THE MOLECULAR STRUCTURE OF RICE-STARCHY SYSTEMS

Abstract

Investigations on the physicochemical property and molecular structure of starches in Taiwan are reviewed in relation to the eating quality of cooked rice. In addition to some conventional indices (i.e. Brabender viscoamylographic indices, gel consistency, and sensory properties), dynamic rheological parameters are also involved to clarify the importance of molecular properties of starch on the eating quality. The samples discussed were isolated from 9 indica, 9 japonica and 4 waxy varieties. The average number degree of polymerization (DP_n) of their amylopectin molecules are in the order of japonica \geq waxy \geq indica; while the average chain length (CL), and average exterior chain length (ECL) are indica \geq waxy \geq japonica. Indica amylopectins, especially from the starches of high amylose contents (AC, > 26%), carry a greater proportion of long chains than the other two varieties. As to amylose, the DP_n and CL values of high-molecular-weight subfractions are somewhat higher for indica amylose than for the japonica. Generally, Brabender viscoamylographic indices of rice flours are well correlated with the apparent AC, gel consistency (GC), and sensory cohesiveness as well as stickiness of cooked milled rice. But the flours with 0-21% AC show similar pasting and soft-gel properties. Dynamic rheological measurements suggest more precisely that different type of starches give their individual rheological patterns during gelatinization and retrogradation, primarily depending on AC and the molecular structure of amylopectin, rather than amylose. Although the AC is commonly regarded as the determinant of eating quality of cooked rice, the molecular and granular structures of starches still give potentially important influences on the physical properties of starchy systems including cooked rice or rice paste.

Introduction

The eating quality of rice (*Oryza sativa* L.) differs remarkably between three categories – indica, japonica and waxy rice [1-2]. Since starch is the principal constitu-

¹ Institute of Chemistry, Academia Sinica, Taipei 115, Taiwan

² Graduate Institute of Food Science and Technology, National Taiwan University, Taipei 107, Taiwan

³ Department of Food and Nutrition, Providence University, Shalu, Taichung 433, Taiwan

⁴ Department of Food Science, National Chung-Hsing University, Taichung 402, Taiwan

* Corresponding author. E-mail: cylu@chem.sinica.edu.tw

ent of milled rice (~90%), diverse varieties of rice starches have been extensively investigated to elucidate the physicochemical basis of rice quality [2-7]. In order to rationalize the cooking or processing method of rice, to classify rice on the basis of eating quality, or to develop preferential rice cultivars, some physicochemical indices have been noticed in relation to rice quality. There are the water absorption, volume expansion and alkali spreading value of milled rice, the instrumental and sensory texture of cooked rice, and the final gelatinization temperature (GT), gel consistency (GC), viscoamylographic parameter, swelling number, hot-water solubilization, and the apparent as well as hot-water-insoluble amylose content (AC) of rice flours or starches [8]. Correlations between these traditional indices and the eating quality of cooked rice have been reviewed by Juliano [8, 9]. And, the classification of rice quality is generally made on the basis of total or hot-water-insoluble AC, GC, GT, viscoamylographic indices, etc. [4-9]. However, the role of these indices and the structures of starch molecules in the texture of rice products are still ambiguous [3, 9]. Recently, the fine structure of rice starch molecules, i.e. amylose and amylopectin, have been extensively examined in our laboratory and elsewhere [10-16], and giving important influences on the pasting and rheological properties during gelatinization and retrogradation of rice starch systems [10, 13, 17-18]. Therefore, the effects of the AC, molecular structure, and swelling-solubility property of rice starches on the pasting, gelling and dynamic rheological properties are sequentially summarized in relation to the eating quality of rice products.

Correlations between the physicochemical properties of rice flours

The physicochemical properties of 22 rice flours in the previous studies [5, 13, 15, 18-28] are summarized in Table 1. Nine indica rice studied include Tainan Sen 15 (TNS15), Tainan Sen 19 (TNS19), Taichung Native 1 (TCN1), Taichung Sen 17 (TCS17), Kaohsiung Sen 7 (KSS7), Tainung Sen 19 (TNU19), Taichung Sen 3 (TCS3), Taichung Sen 10 (TCS10) and Tai Sen 1 (TS1). Nine japonica rice analysed are Kaohsiung 1 (KS1), Tainan 5 (TN5), Tainung 67 (TNU67), Kaohsiung 142 (KS142), Tainan 9 (TN9), Taichung 189 (TC189), Tainung 70 (TNU70), Taigune 9 (TG9) and Taichung 65 (TC65). And, waxy rice examined are two indica waxy rice [Taichung Sen Waxy 1 (TCSW1), Hong Kiao Waxy (HKW)] and two japonica waxy rice [Taichung Waxy 70 (TCW70) and Hsinchu Waxy 4 (HCW4)]. The average apparent AC in starch is in the range of 14–35%, 9.2–20.5% and 0.9–1.4% for the indica, japonica and waxy samples, respectively. The crude protein and fat contents of these flours are 6.9–12.5% and 0.41–1.08%, respectively. And, the gel consistency in 0.2 N KOH is 28–35 mm and 73–100 mm for the flours of 26–35% and 0.9–20.5% amylose, respectively.

Table 1

Some physicochemical properties of rice flours^a

| Type | Variety | App. AC, % ^b | Crude protein, % | Crude fat, % | GC ^c mm | Literature cited |
|----------|------------|-------------------------|------------------|----------------|--------------------|-----------------------|
| Indica | 11. TNS15 | 34.9 | 10.9 | - ^d | 35 | [19,20] |
| | 12. TNS19 | 28.5 | 8.6 | 0.75 | 32 | [21] |
| | 13. TCN1 | 29.0 | 10.7 | 0.79 | 31 | [5,19-20,22] |
| | 14. TCS17 | 28.3 | 11.0 | 0.53 | 28 | [15,18,22-23] |
| | 15. KSS7 | 26.7 | 12.5 | - | 33 | [5,13,18,19-20] |
| | 16. TNuS19 | 26.3 | 8.02 | 0.41 | 30 | [18,24] |
| | 17. TCS3 | 15.6 | 10.6 | | 76 | [5,19-20] |
| | 18. TCS10 | 15.6 | 8.6 | 0.46 | 81-89 | [5,13,15,19-20,22,25] |
| | 19. TS1 | 14.4 | - | - | - | [15] |
| Japonica | 21. KS1 | 20.5 | 10.7 | - | 87 | [19] |
| | 22. TN5 | 17.5 | 8.2 | - | 93 | [5,19-20] |
| | 23. TNu67 | 16.5 | 8.6 | 0.54 | 73-90 | [13,18,19-23,26] |
| | 24. KS142 | 15.6 | - | - | - | [27] |
| | 25. TN9 | 14.5 | - | - | - | [27] |
| | 26. TC189 | 14.3 | 6.9 | 0.75 | 76 | [15,18,25] |
| | 27. TNu70 | 14.0 | - | - | - | [15,18] |
| | 28. TG9 | 12.5 | - | - | - | [15] |
| | 29. TC65 | 9.2 | 9.2 | - | 88 | [5,19-20] |
| Waxy | 31. TCSW1 | 1.35 | 8.68 | 1.08 | 93-100 | [18,21,23] |
| | 32. HKW | 1.18 | - | - | - | [27] |
| | 33. TCW70 | 0.93 | 7.5 | 0.92 | 97 | [18,24,26,28] |
| | 34. HCW4 | 0.87 | - | - | - | [27] |

^a Data presented were means results in literature.^b Weight percentage on dry starch basis.^c Gel consistency in 0.2 N KOH.^d Not determined.

The Brabender viscoamylographic measurements [5, 29-30] have demonstrated that the peak (P) and hot-paste viscosities (H) of indica rice flours (10%) are larger than those of the japonica, and the waxy the least. However, the inverse situation is true for rice starches (7%) [30]. Three indica rice flours (e.g. TNS15, TCN1 and KSS7) have greater setback (SB) and total setback viscosities (SB_t), but lower breakdown ratio (BD_r) than the other samples. The viscoamylographic indices and gel consistency, commonly regarded as the important indicators for eating quality of cooked rice [5,7,8], are closely correlated with AC (Table 2) [5]. Significant correlations between AC, GC, and Amylographic indices of rice flours, and the hardness and stickiness of

cooked rice were also found by Song et al. [2] and Juliano [3, 8]. Nonetheless, most of viscoamylographic indices except for H and SB_t are less correlated with the crude protein content. In the case of gel consistency, it shows significantly negative correlation with the H, SB, SB_t, H/P, and C/P ratios ($p < 0.05$), where C is the cold-paste viscosity [5].

Table 2

Correlation coefficients between physicochemical properties and the Brabender viscoamylographic indices of 10% rice flours [5]

| Indices | Apparent AC | Crude protein content | Gel consistency |
|-----------------|-------------|-----------------------|-----------------|
| P | 0.32 | 0.44 | -0.63 |
| H | 0.82** | 0.67 ^a | -0.89** |
| BD | -0.67 | -0.25 | 0.32 |
| BD _r | -0.90** | -0.62 | 0.64 |
| SB | 0.92** | 0.53 | -0.70* |
| SB _t | 0.98** | 0.67* | -0.88** |
| H/P | 0.87** | 0.53 | -0.72* |
| C/P | 0.89** | 0.50 | -0.68* |
| C/H | 0.75* | 0.40 | -0.45 |

^a Significant level: *, $p \leq 0.05$; **, $p \leq 0.01$; ***, $p \leq 0.001$

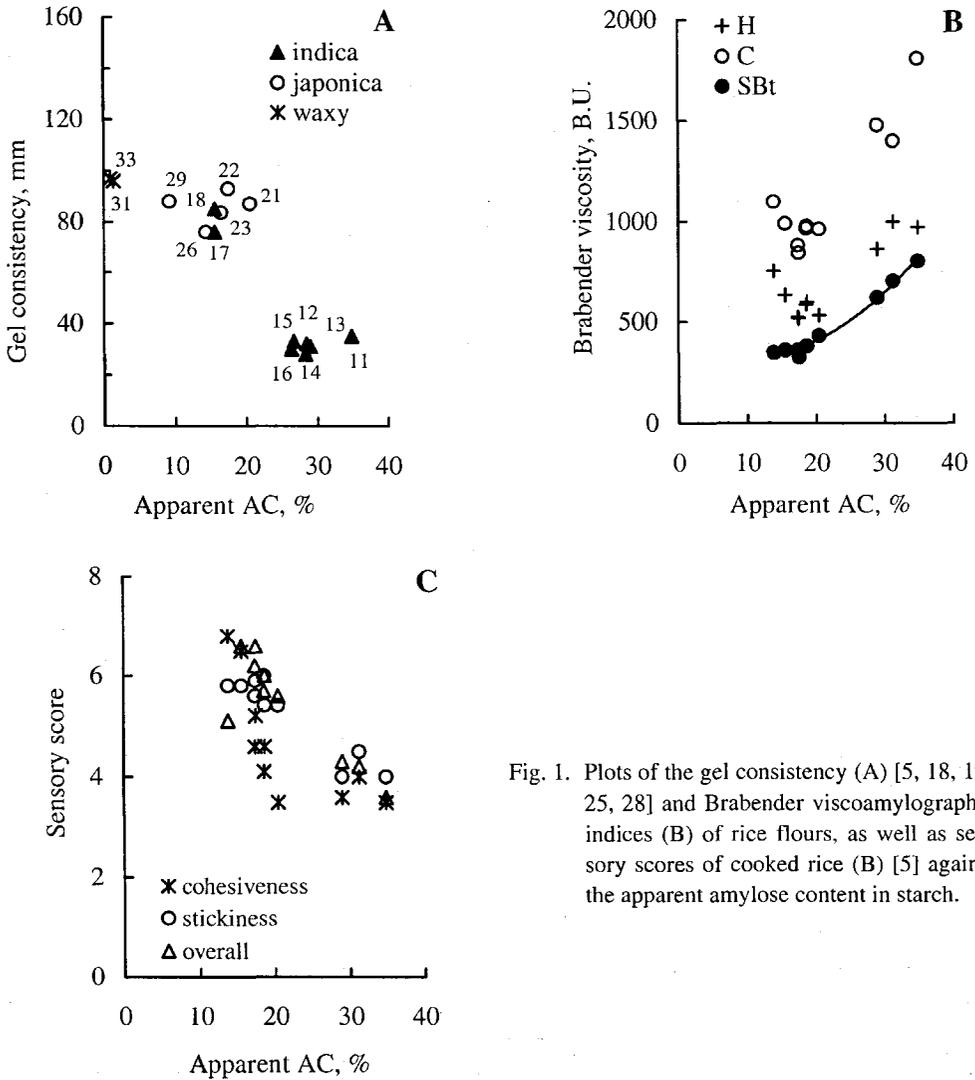
Table 3

Correlation coefficients between the eating quality of cooked milled rice and the physicochemical properties of rice flours [5]

| | Cohesiveness | Stickiness | Overall |
|---------------------------|--------------------|------------|---------|
| Crude protein content | -0.52 | -0.70* | -0.66* |
| Apparent AC | -0.72 ^a | -0.94** | -0.87** |
| Gel consistency | 0.38 | 0.94** | 0.80** |
| Viscoamylographic indices | | | |
| Pasting temperature | -0.29 | -0.66* | -0.63 |
| P | 0.28 | -0.41 | -0.42 |
| H | -0.26 | 0.83** | 0.66* |
| BD | -0.18 | 0.18 | 0.65* |
| BD _r | 0.84** | 0.84** | 0.86** |
| SB | -0.72* | 0.86** | -0.87** |
| SB _t | -0.61 | 0.93** | -0.91** |
| H/P | -0.57 | 0.84** | 0.92** |
| C/P | -0.68* | 0.80** | 0.82** |
| C/H | -0.89** | 0.69* | 0.50 |

^a Significant level: *, $p \leq 0.05$; **, $p \leq 0.01$; ***, $p \leq 0.001$

The above physicochemical properties and the eating quality of cooked milled rice such as cohesiveness, stickiness and overall texture are negatively correlated with ($p < 0.01$) the crude protein and apparent amylose contents, but positively with GC (Table 3) [5]. The significant factors are BD_r , SB, C/P and C/H values for cohesiveness, H, BD_r , SB, SB_t , H/P, C/P and C/H for stickiness, and H, BD, BD_r , SB, SB_t , H/P, and C/P for overall scores.



The Ac-dependencies of the eating quality indices are further depicted in Figure 1. The gel consistency measurements (Figure 1A) [5, 19-25, 28] suggest that the rice flour systems can be divided into hard and soft gels as the AC is $\geq 26\%$ (high-AC) and $\leq 21\%$ (waxy to low-AC) respectively, according to the classification of Juliano [3]. Since the gelling time for GC measurements is short (30 or 60 min) [8], and solely reflecting the properties of short-term retrogradation, it is likely incapable of further identifying the influence of AC and molecular structure. The viscoamylographic indices H, C and SB_t show positive AC-dependence for the high-AC indica flours (Figure 1B) [5]. While, the AC-dependence of paste viscosity can vary with the flour concentration used [31]. In addition, the SB_t value increased with increasing AC ($SB_t = 0.75AC^2 - 13.50AC + 374.85$, $R^2 = 0.99$) due to the effect of water-soluble amylose leaching. This tendency is different from those of BD_r , which decreasing with increasing AC ($BD_r = 0.001AC^2 - 0.110AC + 2.997$, $R^2 = 0.82$). The latter phenomenon could be attributed to the fact that the higher-AC starch granule is more rigid and resistant to swelling and disintegration [6, 7, 17, 26]. As to the sensory properties (Figure 1C) [5], those of low-AC (10-21%) have high scores in cohesiveness, stickiness and overall texture due to the consumer preference [9]. Similarly, Sandhya Rani et al [7] reported that the paste breakdown (BD) of 21 nonwaxy rice flours is inversely correlated to the sensory and viscoelastograph hardness of cooked rice, and the BD at 95°C correlated excellently with total and insoluble AE, sensory and instrumental measures of cooked-rice texture.

Generally, the gelatinized high-AC rice, rice flours or starches show greater firmness, higher cold-pasting viscosity [5, 29], Amylographic consistency, total setback [3, 5], and gel rigidity [3, 17, 32] due to notable retrogradation within granule or to granular rigidity [6-7], as comparing with the low-AC. Accordingly, starch granule rigidity or fragility may be the basic element in rice quality [7]. The texture of cooked rice is primarily governed by the apparent or water-insoluble AC, rather than by crude protein [5, 7-9], in agreement with the findings of Bhattacharya et al. [4]. However, some disagreements are also found as compared with the data of Juliano, who discovering that protein has significant influences on the GC, P, and SB values of rice flours, and the hardness, rather than stickiness, of cooked rice [8].

Correlations between the fine structure and retrogradation property of amylopectin

Fine structure of rice amylopectin

Two typical profiles of size exclusion chromatography (SEC) were found for the chain distribution of 14 rice amylopectins (Figure 2) [14]. The type I profile has three peaks including the extralong chain fraction (a) of chain length (CL) > 100 g.u.), long

chain fraction (b) of CL = 25–100 g.u. and the short chain fraction (c) of CL < 25 g.u.. While the second type (II) only contains the b and c fractions.

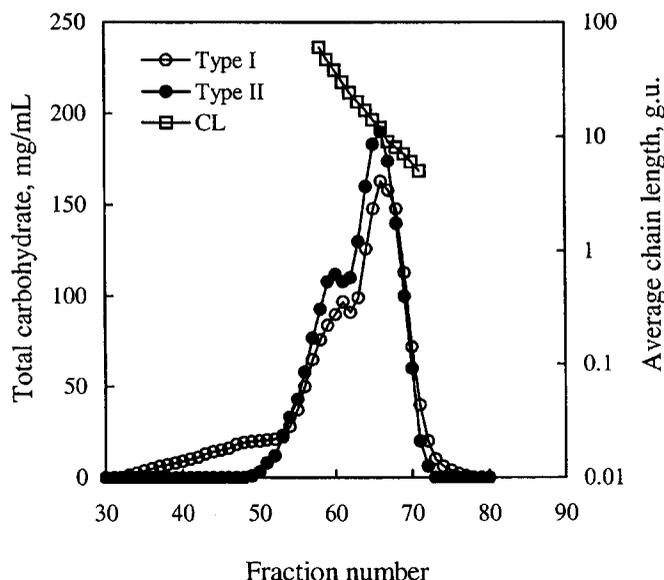


Fig. 2. Molecular chain distributions of rice amylopectins measured by size exclusion chromatography [14].

The molecular properties of 14 amylopectins (APs) from indica, japonica and waxy rice can be obtained from the SEC results, including the molar fractions of a, b, and c, the (a+b)/c ratio, the number-average degree of polymerization (DP_n), average chain length (CL), average exterior chain length (ECL), and average interior chain length (ICL). As indicated in Table 4, three indica amylopectins (TCN1, TCS17 and KSS7) show type I profile carrying 4~11% extralong chains, 29~36% long chains, and 58~65% short chains with (a+b)/c ratios of 0.54–0.71 [14]. The DP_n , CL, ECL and ICL of these three APs are 1743~2885, 20.2~22.1, 14.5~15.8 and 4.7~5.3 g.u., respectively. The other APs give type II profiles with negligible amount of extralong chains, 34~36% long chains and 64~66% short chains with (a+b)/c ratios 0.51-0.56. And, the DP_n , CL, ECL and ICL are 6481~11931, 15.4~19.8, 11.3~13.4, and 3.2~5.7 g.u., respectively. Generally, the DP_n value is indica \leq waxy \leq japonica; the CL and ECL, indica \geq waxy \geq japonica; and the ICL similar for three varieties of APs. The above results are consistent with those of Reddy et al. [11] that the APs from the highest-amylose-equivalent (AE) variety have the largest proportion of long B chains in the exterior region and the lowest proportion of short chains, while the reverse was true for waxy rice. By studying on 8 varieties of rice AP fractions, Huzukuri and his coworkers [33]

also displayed that the CL values of indica rice APs (20–22 g.u.) are slightly greater than those of the japonica (19–20 g.u.), and indica APs having greater molecular sizes. Nonetheless, Juliano found that the nonwaxy and waxy rice APs have similar ratios of A to B-chains [3].

Table 4

Chain distributions and molecular properties of amylopectins from various rice starches ^a [14]

| Variety | Extralong, a % ^b | Long b % ^b | short c % ^b | Chain ratio, (a+b)/c | DP _n g.u. | CL g.u. | ECL g.u. | ICL g.u. |
|-----------|--------------------------------|--------------------------|---------------------------|-------------------------|-------------------------|------------|-------------|-------------|
| 13. TCN1 | 10.1 | 31.4 | 58.5 | 0.71 | 2827 | 22.1 | 15.8 | 5.3 |
| 14. TCS17 | 10.9 | 29.2 | 59.9 | 0.67 | 2885 | 21.7 | 15.4 | 5.3 |
| 15. KSS7 | 3.7 | 35.6 | 60.7 | 0.65 | 1743 | 20.2 | 14.5 | 4.7 |
| 18. TCS10 | nd ^c | 36.2 | 63.9 | 0.57 | 6481 | 18.8 | 13.4 | 4.3 |
| 19. TS1 | nd | 34.9 | 65.1 | 0.54 | 7850 | 18.5 | 13.2 | 4.2 |
| 23. TNU67 | nd | 34.5 | 65.5 | 0.53 | 8812 | 17.5 | 12.6 | 3.9 |
| 24. KS142 | nd | 34.3 | 65.7 | 0.52 | 7327 | 17.3 | 12.2 | 4.1 |
| 25. TN9 | nd | 34.5 | 65.5 | 0.53 | 9540 | 16.3 | 11.7 | 3.6 |
| 26. TC189 | nd | 35.0 | 65.1 | 0.54 | 10470 | 15.4 | 11.3 | 3.2 |
| 27. TNU70 | nd | 35.4 | 64.6 | 0.55 | 11931 | 15.7 | 11.5 | 3.2 |
| 31. TCSW1 | nd | 35.7 | 64.3 | 0.56 | 7721 | 19.8 | 13.1 | 5.7 |
| 32. HKW | nd | 35.0 | 65.0 | 0.54 | 8270 | 19.1 | 13.2 | 4.8 |
| 33. TCW70 | nd | 34.2 | 65.8 | 0.52 | 9101 | 17.6 | 12.2 | 4.4 |
| 34. HCW4 | nd | 33.9 | 66.1 | 0.51 | 9844 | 17.4 | 11.8 | 4.6 |

^a Means with different letters in the same column are significantly different ($p < 0.05$)

^b Molar percentage determined by SEC.

^c Not detectable

Influence of amylopectin structure on the retrogradation property itself

It is known that the hardness or gel strength of starch gels or cooked rice is proportional to the retrogradation enthalpy. And, the changes in the retrogradation enthalpy of AP gels can be described according to the Avrami equation [34]:

$$\log\{-\ln[(\Delta H_{\infty}-\Delta H_t)/(\Delta H_{\infty}-\Delta H_0)]\} = \log k + n \log t$$

where k is the rate constant, and n is the Avrami exponent implying the geometry of crystallites [35]. The double logarithmic Avrami plots of TCS17 (indica), KS142 (japonica) and TCSW1 (waxy) AP gels (60%) are exemplified in Figure 3 [36]. Obviously, a two-stage retrogradation process was suggested with a slope deviating at the first 7th day of storage at 5°C. Such kind of two-stage retrogradation behavior was also found in potato starch gels [37]. The slope (n_1) of short-term retrogradation (I) is

TCS17 < TCSW1 < KS142, and those (n_{II}) of the long-term (II) TCS17 \approx TCSW1 < KS142.

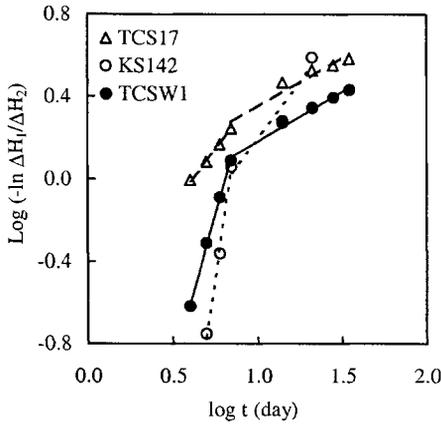


Fig. 3. Changes in the retrogradation enthalpy of 60% rice amylopectin with aging time (at 5°C) according to the double logarithmic form of Avrami equation. ($\Delta H_1 = \Delta H_\infty - \Delta H_t$, $\Delta H_2 = \Delta H_\infty - \Delta H_0$, and ΔH_0 , ΔH_t and ΔH_∞ are the retrogradation enthalpy changes at 0, t and infinite ($t \rightarrow \infty$) days of storage, respectively) [36].

Correlation coefficients between the n_I , k_I , n_{II} and k_{II} values and the molecular properties of AP are tabulated in Table 5 [36]. For the short-term retrogradation stage the n_I value significantly increased with increasing the molar fraction of short chain (c) and DP_n , and with decreasing the molar fraction of extralong chain (a), and (a+b)/c ratio, CL, ECL, and ICL. The k_I value increases with increasing the molar fraction of extralong chain (a), (a+b)/c ratio, CL, and ECL, and with decreasing the molar fraction of short chain (c) as well as DP_n . For the long-term retrogradation stage (II), the above molecular properties give insignificant influences on the n_{II} ; but increasing the a value or decreasing b value results in the greating k_{II} significantly.

Table 5

Correlation coefficients between the two-stage retrogradation characteristics and molecular properties of rice amylopectins^a [36]

| Properties | Short-term (stage I) | | Long-term (stage II) | |
|------------------------|----------------------|--------|----------------------|----------|
| | n_I | k_I | n_{II} | k_{II} |
| Extralong chain (a), % | -0.64* | 0.70* | -0.40 | 0.59* |
| Long chain (b), % | 0.41 | -0.58 | 0.46 | -0.65* |
| Short chain (c), % | 0.72* | -0.68* | 0.29 | -0.44 |
| (a+b)/c ratio | -0.71* | 0.68* | -0.29 | 0.44 |
| DP_n , g.u. | 0.75**b | -0.72* | 0.16 | -0.36 |
| CL, g.u. | -0.79** | 0.61* | -0.32 | 0.42 |
| ECL, g.u. | -0.82** | 0.66* | -0.24 | 0.40 |
| ICL, g.u. | -0.64* | 0.44 | -0.45 | 0.40 |

^a Retrogradation levels determined by DSC on 60% amylopectin systems.

^b Significant level: *, $p \leq 0.05$; **, $p \leq 0.01$; ***, $p \leq 0.001$

Obviously, the molecular structure and chain distribution of APs significantly governs the geometry of crystallites and the retrogradation rate during short-term storage. While, the molecular chain distribution still influences the retrogradation rate of long-term storage. As comparing the results of Table 4 with the Table 1 and Figure 1, it is found that the high-AC rice (e.g. TCN1, TCS17 and KSS7), which having hard-gel property, high viscosity, and low stickiness, possesses the AP of a lower DP_n , higher CL and ECL, and higher $(a+b)/c$ ratio, as compared with the low-AC. And, the proportion of extralong and long chains of AP would contribute greatly to the hardness caused by short-term retrogradation of the parent starch, flour or cooked rice. Based on the results of 8 varieties rice starch, Juliano and his coworkers [3, 38] also showed that the APs of waxy rices with high GT ($\geq 75^\circ\text{C}$) have larger molecular weights than those of rices with low GT. Hence, the harder texture of cooked rice products from high-GT waxy rices may be due to the higher molecular weight of their APs. Similarly, Shi and Seib [39] observed that AP retrogradation is directly proportional to the fraction of DP 16–30, and inversely to the fraction of DP 6–11. They also attributed a higher onset melting temperature and retrogradation enthalpy to a greater proportion of long chains ($DP > 16$) in the AP [39]. The positive correlation between the n_1 and c value is consistent with the findings of Mua and Jackson [40, 41] that the corn AP with an intermediate to low M_w shows a marked retrogradation. Since the retrogradation enthalpy of starch is proportional to the amylopectin content and hardness [42], the above results further confirm the importance of the AP structure in the eating quality of cooked rice or rice products.

Correlations between the fine structure of amylose and the physical property of parent starches

Fine structure of rice amylose

Generally, rice amylose (AM) consists of 40–67 wt% linear and 33–60 wt% branched fractions [9]. The molecular properties of AM molecules fractionated from Taiwan indica and japonica rice were examined by size-exclusion chromatography and are tabulated in Table 6 [13, 15–16], where the F1 and F2 represent high and low-molecular-weight subfractions respectively. It is shown that the DP_n and CL are in the range of 987~1225 and 276~430 g.u., respectively, for both indica and japonica AMs. These results are somewhat different from those of Hizukuri and his coworkers [12, 43, 44] on 7 varieties of AMs from other rice cultivars, of which the DP_n is 532–910 g.u. (linear chains) or 1130–1660 g.u. (branched chains) and the CL 101–250 g.u, depending on the recrystallization condition [12]. In addition, the DP_n and CL of sub-fraction F1 (Table 6) appear to be fairly higher for the indica AM (1486~2011 and

324–385 g.u.) than for the japonica (1472~1696 and 247~317 g.u. respectively). While, the DP_n and CL of subfraction F2 (353–441 g.u. and 152–309 g.u. respectively) are comparable for both varieties. These results are also somewhat different from the data of Hizukuri [50] that the DP_n and CL are 2230 and 330 g.u. for the F1, 1670 and 520 g.u. for the F2, and 410 and 295 g.u. for the F3 subfraction, respectively. Among the AM molecules examined, the CL of indica AMs is not certainly greater than the japonica, also disagreeing with the reports of Juliano [9].

Table 6

Molecular properties of rice amylose fractions and subfractions ^a

| Variety | Whole AM | | F1 subfraction | | F2 subfraction | |
|-----------|----------|-----|----------------|-----|----------------|-----|
| | DP_n | CL | DP_n | CL | DP_n | CL |
| 13. TCN1 | 1135 | 335 | 2011 | 347 | 378 | 252 |
| 14. TCS17 | 1225 | 276 | 1623 | 324 | 353 | 168 |
| 15. KSS7 | 1075 | 430 | 1486 | 364 | 436 | 291 |
| 18. TCS10 | 1160 | 393 | 1776 | 385 | 437 | 309 |
| 19. TS1 | 1157 | 402 | 1665 | 340 | 409 | 241 |
| 23. TNu67 | 1004 | 287 | 1472 | 294 | 441 | 152 |
| 26. TC189 | 1114 | 333 | 1696 | 298 | 373 | 266 |
| 27. TNu70 | 1204 | 365 | 1533 | 247 | 447 | 248 |
| 28. TG9 | 987 | 332 | 1578 | 317 | 401 | 267 |

^aData in glucose unit were obtained from [13, 15-16].

Influence of amylose structure and swelling-solubility property on the rheological property of starch

Since the $\tan \delta$ and G' values are highly correlated with the stickiness and hardness of cooked rice [45], correlating the dynamic rheological and swelling-solubility properties of starch systems (30%) [18] to the molecular properties of amylose fractions [13, 15-16] were interested. Table 7 exhibits that the swelling power (SP), storage modulus and loss tangent at 95°C (G'_{95} and $\tan \delta_{95}$) during gelatinization, and the G' and $\tan \delta$ at 25°C (G'_{25} and $\tan \delta_{25}$) as well as the exponent ($n_{G'_{25}}$) of starch concentration ($G'_{25} \propto C^n$) on retrogradation are significantly correlated with AC. Increasing AC tends to reduce the SP, $\tan \delta_{95}$ and $\tan \delta_{25}$ ($p < 0.05$), and to increase the G'_{95} , G'_{25} and $n_{G'_{25}}$ ($p < 0.01$). Interestingly, these rheological parameters are insignificantly correlated with the DP_n and CL of amylose and its subfractions. And, the water soluble index (WSI) on gelatinization is mainly influenced by the DP_n of F2 subfraction (low- DP fraction), instead of AC. The lower the DP_n of F2, the higher is the WSI.

Table 7

Correlation coefficients between the physical properties of rice starches and the molecular properties of their amylose fractions ^a

| Property | Gelatinization | | | | Retrogradation | | |
|----------------------|----------------------|--------------------|---------------------|--------------------|---------------------|--------------------|--------------------------------|
| | SP | WSI | G' ₉₅ | tan δ_{95} | G' ₂₅ | tan δ_{25} | n _{G'25} ^b |
| AM content | -0.82 ^{**c} | 0.57 | 0.90 ^{***} | -0.71 [*] | 0.90 ^{***} | -0.74 [*] | 0.88 ^{**} |
| AM-DP _n | -0.11 | -0.11 | 0.06 | -0.46 | -0.08 | 0.09 | -0.12 |
| AM-CL | 0.04 | -0.66 | -0.38 | -0.14 | -0.27 | 0.12 | -0.67 |
| AMF1-DP _n | -0.41 | 0.48 | 0.38 | 0.23 | -0.28 | 0.20 | -0.36 |
| AMF1-CL | -0.56 | -0.07 | 0.32 | -0.24 | 0.32 | -0.45 | -0.09 |
| AMF2-DP _n | 0.19 | -0.83 [*] | -0.57 | 0.19 | -0.37 | 0.35 | -0.54 |
| AMF2-CL | 0.13 | -0.53 | -0.38 | -0.14 | -0.41 | 0.20 | -0.75 |

^a Correlation coefficients obtained by correlating the data of [15, 16] to the [18].

^b Exponents of starch concentration ($G'_{25} - C^n$) relationships, where C is starch concentration.

^c Significant level: * $p \leq 0.05$; ** $p \leq 0.01$; *** $p \leq 0.001$.

Sharp [44] has present close relationships between the rapid viscosity analyzer (RVA) and standard Bradender viscoamylographic indices. Hence, the correlation between RVA parameters of starch systems (8%) [18] and the molecular property of amyloses [15-16] as well as the swelling-solubility property of starch itself [18] were analyzed. The RVA parameters examined (Table 8) include T_o (onset temperature of viscosity increase), T_p (temperature of peak viscosity), P (paste viscosity at 95°C), H (holding viscosity at 95°C for 4 min), P-H (difference between P and H), C (cold viscosity at 35°C), C-H (difference between C and H) and F (final viscosity at 35°C for 5 min). And, the swelling-solubility properties of rice starch systems (1%) at 95°C include SP (swelling power), WSI (water soluble index), BV (blue value) and λ_{max} (maximum wavelength). The apparent AC, ins. AC (hot-water-insoluble AC) and lipid-AC (the amount of amylose binding with lipid) [18] were also involved. The correlation coefficients (Table 8) suggest that the AC, ins. AC, lipid-AC and swelling-solubility properties gives significant effects on most of the RVA parameters. But, the molecular structure of amylose and its subfractions give a negligible effect on the RVA properties, in agreement with the dynamic rheological parameters. This implies that the swelling property of starches, which principally caused by AP molecules, is more important for the rheological characteristics and consequently texture of rice starch systems.

Table 8

Correlation coefficients between rapid viscosity analyzer indices and physicochemical properties of rice starches^a

| Property | T _o | T _p | P | H | P-H | C | C-H | F |
|----------------------|--------------------|----------------|--------|-------|---------|---------|---------|---------|
| App. AC | 0.69* ^b | 0.71* | -0.56 | 0.61 | -0.88** | 0.88** | 0.89** | 0.89** |
| Ins. AC | 0.60 | 0.63 | -0.53 | 0.52 | -0.81** | 0.90*** | 0.93*** | 0.91*** |
| Lipid-AC | 0.76* | 0.96*** | -0.75* | 0.20 | -0.86** | 0.68* | 0.75* | 0.68* |
| AM-DP _n | 0.19 | 0.85* | 0.56 | 0.59 | 0.24 | 0.53 | 0.46 | 0.48 |
| AM-CL | 0.49 | -0.12 | -0.12 | 0.03 | -0.24 | 0.06 | 0.05 | 0.02 |
| AMF1-DP _n | -0.06 | 0.05 | 0.67 | 0.41 | 0.65 | -0.02 | -0.15 | -0.07 |
| AMF1-CL | 0.71 | -0.42 | 0.13 | 0.45 | -0.32 | 0.47 | 0.44 | 0.47 |
| AMF2-DP _n | -0.15 | -0.30 | -0.59 | -0.58 | -0.32 | -0.36 | -0.27 | -0.35 |
| AMF2-CL | 0.41 | -0.34 | 0.46 | 0.29 | 0.42 | -0.13 | -0.27 | -0.23 |
| SP | -0.69* | -0.97*** | 0.72* | -0.30 | 0.89** | -0.73* | -0.78* | -0.73* |
| WSI | 0.34 | 0.53 | -0.38 | 0.26 | -0.52 | 0.74* | 0.81** | 0.75* |
| BV | 0.66 | 0.94*** | -0.77* | 0.17 | -0.87** | 0.67* | 0.75* | 0.68* |
| λ _{max} | 0.67* | 0.98*** | -0.73* | 0.17 | -0.83** | 0.63 | 0.70* | 0.63 |

^aCorrelation coefficients obtained by correlating the data of [15-16] to [18].

^bSignificant level: * $p \leq 0.05$; ** $p \leq 0.01$; *** $p \leq 0.001$

Conclusion

Generally, the apparent AC or hot-water-insoluble AC has notable effects on the rheological properties and texture of rice starches, flours and rice products. However, the granular rigidity, which resulting from the arrangement of AP and AM molecules, appears to be another important factor responsible for the change in the rheological and eating characteristics. Between these two molecules, the molecular structure of AP shows a more close correlation to the rheological properties interested, possibly due to that AP is the principal component of starch. However, for the pasting property of rice starches and flours, AM and AP molecules would be of the same importance, since the combination of longer-chain AP and the intermediate-molecular-weight AM may synergistically increase the pasting viscosity as in the case of corn starch [47]. Nonetheless, since the gelatinization and retrogradation mechanisms of starches are quite complicated, further studies on the relationships between the granular structure of starch composite and the dynamic rheological indices as well as the eating quality of rice products are required.

REFERENCE

- [1] Juliano B.O.: Starch: Chemistry and Technology, 2nd ed., Academic Press, New York, 1984, 507-528.
- [2] Song S., Hsu A.-N., Hong M.-C.: Rice Grain Quality. Proc. Symp. TDAIS, S. Song and M.-C. Hong, eds. Taichung District Agricultural Improvement Station, Changhua, Taiwan, 1988.
- [3] Juliano B.O.: J. Jap. Soc. Starch Sci., **29**, 1982, 305-317.
- [4] Bhattacharya K.R., Sowbhagya C.M., Indudhara Swamy Y.M.: J. Food Sci., **47**, 1982, 564-569.
- [5] Lii C.-Y., Chang Y.-H.: Symposium of rice quality in Taiwan, 1988, 31-43.
- [6] Radhika Reddy K., Subramanian R., Zakiuddin Ali S., Bhattacharya K.R.: Cereal Chem., **71**, 1994, 548-552.
- [7] Sandhya Rani M.R., Bhattacharya K.R.: J. Text. Stud., **26**, 1995, 587-598.
- [8] Juliano B.O.: Rice: Chemistry and Technology, 1985, 443-524.
- [9] Juliano B.O.: Cereal Foods World, **43**, 1998, 207-221.
- [10] Chinnaswamy R., Bhattacharya K.R.: Starch/Stärke, **38**, 1986, 51-57.
- [11] Radhika Reddy K., Zakiuddin Ali S., Bhattacharya K.R.: Carbohydr. Polym., **22**, 1993, 267-275.
- [12] Hizukuri S., Shirasaka K., Juliano B.O.: Starch/Stärke, **35**, 1983, 348-350.
- [13] Tseng Y.-H.: MS thesis. National Taiwan University, Taiwan, 1996.
- [14] Lu S., Chen L.-N., Lii C.-Y.: Cereal Chem., **74**, 1997, 34-39.
- [15] Huang R.-M., Tseng J.-Y., Lii, C.-Y.: Food Sci. (Chinese), **25**, 1998a, 210-221.
- [16] Huang R.-M., Tseng J.-Y., Lii C.-Y.: Food Sci. (Chinese), **25**, 1998b (accepted).
- [17] Lii C.-Y., Lai M.-F., Tsai M.-L.: Food. Technology. Quality. (Poland), **2** (7), 1996, 27-53.
- [18] Tsai M.-L.: Ph.D. dissertation. National Taiwan University, Taiwan, 1997.
- [19] Lii C.-Y. Chang S.M., Yang H.L.: Bull. Inst. Chem., Academia Sinica, **33**, 1986, 55-62.
- [20] Chang S.-M., Lii, C.-Y.: Bull. Inst. Chem., Academia Sinica, **32**, 1985, 57-61.
- [21] Wu et al.: J. Chinese Agric. Chem. Soc., **30**, 1992, 337-348.
- [22] Huang R.-M., Lii C.-Y.: J. Chinese Agric. Chem. Soc., **28**, 1990, 267-275.
- [23] Lu S., Wu S.-J., Lii C.-Y.: Food Sci. (Chinese), **15**, 1988, 280-286.
- [24] Huang R.-M., Lii, C.-Y.: Cereal Chem., **71**, 1994, 202-207.
- [25] Lin S.-Y., Lii, C.-Y.: J. Chinese Agric. Chem. Soc., **33**, 1995, 482-493.
- [26] Lii C.-Y., Shao Y.-Y., Tseng K.-H.: Cereal Chem., **72**, 393-400.
- [27] Council of Agriculture, Executive Yuan: Rice Varieties in Taiwan, Taiwan, 1987.
- [28] Lin S.-Y., Lii, C.-Y.: Food Sci. (Chinese), **22**, 1995, 407-418.
- [29] Yang C.-C., Lai H.-M., Lii C.-Y.: Food Sci. (Chinese), **14**, 1987, 212-221.
- [30] Chang Y.-H., Chu L.-W., Su N.-C.: Food Sci. (Chinese), **23**, 1996, 739-751.
- [31] Sandhya Rani M.R., Bhattacharya K.R.: J. Texture Stud., **20**, 1989, 127-137.
- [32] Lii C.-Y., Tsai M.-L., Tseng K.-H.: Cereal Chem., **73**, 415-420.
- [33] Hizukuri S.: Carbohydrates in Food, New York., 1996, 347-429.
- [34] Avrami M.: J. Chem. Phys., **8**, 1940, 212-224.
- [35] Sperling L.H.: Introduction to Physical Polymer Science, New York, 1993, 232-235.
- [36] Lii C.-Y., Lu S., Lai V. M.-F., Chen L.-N.: J. Cereal Sci. (submitted).
- [37] Mita T.: Carbohydr. Polym., **17**, 1992, 269-276.
- [38] Juliano B.O., Villareal, R.M.: Starch/Stärke, **39**, 1987, 298-301.
- [39] Shi Y.-C., Seib, P.A.: Carbohydr. Polym., **26**, 1995, 141-147.
- [40] Mua J.P., Jackson D.S.: J. Agric. Food Chem., **45**, 1997, 3848-3854.
- [41] Mua J.P., Jackson D.S.: J. Cereal Sci., **27**, 1998, 157-166.
- [42] Wootton M., Mahdar D.: Starch/Stärke, **45**, 1993, 295-299.

- [43] Takeda Y., Hizukuri S., Juliano B.O.: *Carbohydr. Res.*, **148**, 1986, 299-308.
[44] Hizukuri S., Takeda Y., Maruta N., Juliano B.O.: *Carbohydr. Res.*, **189**, 1989, 227-235.
[45] Ootobe K., Naito S., Sugiyama J., Kikuchi Y.: *Nippon Shokuhin Kagaku Kaishi*, **42**, 1995, 748-755.
[46] Sharp R.N.: *Cereal Chem.*, **63**, 1986, 325-326.
[47] Jane J., Chen J.F.: *Cereal Chem.*, **69**, 1992, 60-65.

KORELACJA MIĘDZY WŁAŚCIWOŚCIAMI FIZYCZNYMI, SMAKOWITOŚCIĄ I STRUKTURĄ CZĄSTECZKOWĄ SKROBI RYŻOWEJ

Streszczenie

Dokonano przeglądu badań nad fizykochemicznymi właściwościami i strukturą cząsteczkową skrobi tajwańskich i odniesiono wyniki tych badań do smakowitości gotowanego ryżu. Aby wyjaśnić związek pomiędzy strukturą cząsteczkową skrobi a smakowitością poza takimi zwykłymi wskaźnikami jak parametry charakterystyki kleikowania Brabendera, konsystencją żelu i właściwościami sensorycznymi wzięto pod uwagę parametry z dynamicznych pomiarów reologicznych. Próbki skrobi wyodrębniono z 9 odmian ryżu indica, 9 odmian japonica i 4 skrobi woskowych. Średni stopień polimeryzacji (DP_n) ich cząsteczek amylopektyny układał się w szeregu japonica > woskowa > indica, podczas gdy średnia długość łańcucha (CL) i średnia zewnętrzna długość łańcucha (ECL) malały w szeregu indica > woskowa > japonica. Amyloektyna z odmian indica, szczególnie ze skrobi wysokoamylozowych (AC > 26%) miały większy udział łańcuchów długich niż amylopektyna z pozostałych odmian. Natomiast dla amylozy, DP_n i CL wysokocząsteczkowych podfrakcji są nieco wyższe w przypadku odmian indica niż odmian japonica. Ogólnie, parametry charakterystyki kleikowania dla mąk ryżowych dobrze korelują z pozorną zawartością amylozy, AC, GC i sensoryczną kohezynnością oraz skleikowatością gotowanego zmielonego ryżu. Jednak mąki o AC 0–21% podobnie kleikowały i a ich żele miały podobną miękkość. Dynamiczne pomiary lepkości lepiej pokazują, że różne rodzaje skrobi mają swe indywidualne charakterystyki reologiczne w czasie kleikowania i retrogradacji. Zależą one przede wszystkim od AC i struktury cząsteczkowej amylopektyny, a mniej od struktury amylozy. Chociaż AC powszechnie uważa się za wyznacznik smakowitości gotowanego ryżu struktury cząsteczkowa i gałeczkowa wciąż w istotny sposób wpływają na fizyczne i właściwości układów skrobiowych z gotowanego ryżu i pasty ryżowej. ☒