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STUDIES ON STARCH GELATINIZATION AND RETROGRADATION WITH DYNAMIC RHEOMETRY – THE INFLUENCE OF STARCH GRANULAR STRUCTURE AND COMPOSITION

Abstract

The study on the starch gelatinization and retrogradation with dynamic rheometry are reviewed. Three typical varieties of rice starches, including indica (KSS7), japonica (TNu67) and waxy rice (TCW70) are used during the discussion. The amylose contents are 24-26 % for KSS7, 15-16 % for TNu67, and 0.8-1.0 % for TCW70. The heating and cooling behaviours of the individual starch, the combination of two starches, and the addition of amylose to the starch systems are discussed.

The correlation between swelling power, amount of water soluble, blue value, and λ_{max}, as well as gelatinization temperature, and the dynamic rheogram are applied for the elucidation of relationships between the starch molecular and granular structures, and the gelatinization and the retrogradation mechanisms. Generally, the G' increases in gelatinization process of starch is mainly governed by the granular characteristics, which include the rigidity of swollen granule and the interaction between these close-packed granules. However, the G' in starch retrogradation is influenced by the interaction between leached-out or external added amylose itself and swollen granule, in addition to the property of swollen granule. As for the mixed starch system, the combination of waxy and non-waxy starches will decrease G' drastically. Whereas the addition of amylose molecule will decrease the G' for the gelatinization process, but will increase G' during cooling and aging profoundly. Hence, it is suggested that the starch granular properties and characteristics are the major factor for the starch rheological behavior, followed by the leached-out amylose during gelatinization process, especially in the high concentration system.

Introduction

Changes in physicochemical properties of starchy product are usually described by the gelatinization and retrogradation behaviours of starch. When the aqueous starch suspension is heated above the gelatinization temperature, an irreversible swelling will occur. This irreversible swelling is accompanied by the loss of order, the loss of crystallinity, and the release of amylose into solution [1-4]. Starch gelatinization in excess

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water has been considered as a two-stage process, consisting of the initial swelling of the granule and its eventual dissolution. Such behavior follows pseudo-first-order Arrhenius kinetics [5]. At sufficient concentration, the hot starch suspension will behave as a viscoelastic dispersion [6-8]. During cooling, the paste may be transformed into an opaque elastic gel [3, 9-11]. The SEM for starch paste or gel indicates a coarse network formed by the solubilized amylose and amylose-linked swollen granules [12]. Thus, the paste and the gel are often considered as a composite material with the swollen starch granules filling through the polymer solution [9-11, 13-17]. Miles and his co-workers have suggested that the initial stages of gelation of starch is dominated by the gelation of the solubilized amylose [10]. However, the results from Evans and Haisman (1979) showed that the material outside the swollen granules (eg. amylose) had little effect on the rheology of the starch suspensions [18]. Factors influencing on the rheological properties of starch gel or paste include the starch granules (concentration, granule size and distribution, swelling pattern, rigidity and deformability of granule) [7, 19-22], amylopectin (fine structure) [23-26], leached-out amylose (amount, type and entanglements), interactions between the components (granule-granule contact and granule-amylose interactions) [25, 27], temperature, heating and cooling rates, mechanical treatments [6-8, 19], additives, etc. The structure of gel or paste controls the texture and quality of starchy foods.

Many studies concerning these behaviours have been made using differential scanning calorimetry, Brabender viscoamylography, x-ray diffractometry, β-amylase-pullulanase method [28-31], etc. However, parts of studies on gelatinization and retrogradation behaviour observed from change in viscosity of starch dispersion involved the behaviour of highly sheared starches with extensively disrupted granule. It is important to explore the contribution of leached-out amylose chain, swollen granule and the interaction through the system on the starch rheology with an undamaged, precise and simultaneous approach. Recently, a small angle oscillatory rheometer has been adopted as one of excellent tools, because it provides information about the rapid change of viscoelastic properties of starch dispersion during heating and cooling with negligible interference on the formation of a gel network [6, 8, 20, 22, 27, 32-40]. Hence, the effect of molecular and granular structures of rice starch on the dynamic rheological properties of starch dispersion system during heating and cooling are reviewed, in order to clarify the mechanisms of starch gelatinization, gelation, and retrogradation.

Pyysical and structural characteristics of rice starch

Rice (*Oryza sativa* L.) can be classified into three categories – indica, japonica and waxy rice [41]. Hsieh and his co-worker [42] indicated that the granular sizes of both indica and japonica rice starches were 2~10 μm; and waxy rice starch, 2~8 μm. The mean sizes of these starches are in the range of 4~5 μm. Rice starch is polygonal in shape [42, 43-44]. The apparent amylose contents in starches from indica, japonica and waxy varieties are in the ranges of 14~29 %, 14~19%, and 0.8~2.0 %, respectively [8, 22, 45]. The powdered X-ray diffractogram of rice as well as other cereal starches shows a typical A-type [28].

Studies on the gelatinization temperatures (GT) for various rice starches by DSC measurements indicate that no significant differences are observed among these three varieties. The result implies that the GT of rice starch may be principally governed by the starch granular structure and by the chain length of amylopectin rather than by the amylose content [44-46]. Brabender viscoamylograms of all non-waxy rice starches display a moderate restricted-swelling pattern [44] and belong to type-B according to Schoch's classification [47]. And the setback viscosity have a close correlation with the amylose content. A type-A viscoamylogram with a high pasting peak is shown for the waxy variety.

Table 1

Molecular characteristics and some physical properties of rice starches

		Indica KSS7	Japonica TNu67	Waxy TCW70
Amylose (%)[a]		24.1~25.6	14.8~15.7	0.78~0.99
DP_n[b]		1075	1004	–[g]
Amylopectin DP_n[c]		2743	8812	9101
Physical property				
	WBC, %[d]	93	118	–
	Iodine affinity, %[d]	4.95	3.73	–
	Gelatinization[e]			
	T_o-T_p-T_c, °C[f]	72.0-76.6-89.2	64.4-71.0-82.3	64.0-71.9-85.0
	ΔH, cal/g	3.37	2.94	3.20
	Retrogradation			
	ΔH, J/g	~10	~9.0	~8.0

[a] apparent amylose content was determined by the method of Lii et al. (61)
[b] exerpted from ref. 48
[c] excerpted from ref. 45
[d] excerpted from ref. 49
[e] excerpted from ref. 8 & 22
[f] T_o, T_p, T_c, and ΔH designated for the onset, peak, and completion temperatures; and the enthalpy for gelatinization
[g] not detected

The compositions and physical properties of three typical rice starches, including indica (Kaohsiung Sen 7, KSS7), japonica (Tainung 67, TNu67) and waxy (Taichung waxy 70, TCW70) varieties, are excerpted from the investigations of Chen [45], Lii and his co-workers [8, 22, 45, 48, 49, 62] and are listed in Table 1. Apparent amylose contents of KSS7, TNu67 and TCW70 are 24~26 %, 15~16 % and 0.8~1.0 %; and the number-averaged degree of polymerization (DP_n) of the KSS7 and TNu67 amyloses are 1075 and 1004 (glucose units) [48], respectively. And, the DP_n of KSS7, TNu67, and TCW70 amylopectins are 2743, 8812, and 9101, respectively [45]. Indica starch possesses lower water binding capacity (WBC) than that of japonica starch [49]. And, the temperatures and enthalpies of gelatinization measured with DSC are 72~89°C and 3.37 cal/g for KSS7; 64~82°C and 2.94 cal/g, TNu67; and 64~85°C and 3.20 cal/g, TCW70 [8, 22]. The retrogradation enthalpies for 20 % concentration (w/w) stored at 5°C are KSS7 > TNu67 > TCW [45]. Generally, the high-amylose KSS7 starch possesses the amylopectin with significantly lower DP_n, higher iodine affinity, higher gelatinization temperature and retrogradation enthalpy than the other two starches.

Table 2

Structural properties of rice amylopectins [45]

		Indica KSS7	Japonica TNu67	Waxy TCW70
Average chain length, $\overline{CL}$	(g.u.)	20.2	17.5	17.6
Exterior chain length, $\overline{ECL}$	(g.u.)	14.5	12.6	12.2
Interior chain length, $\overline{ICL}$	(g.u.)	4.67	3.86	4.39
β-Amylolysis limits (%)		62.1	60.8	58.0
Chain distribution[a] (%)	Extralong (a)	3.74	nd[b]	nd
	Long (b)	35.6	34.5	34.2
	Short (c)	60.7	65.5	65.8
	(a+b)/c	0.648	0.527	0.519
λ_{max} (nm)		592	538	533

[a] measured with GPC
[b] not detectable

The structural properties of these three rice amylopectins are listed in Table 2 [45]. The average chain length ($\overline{CL}$), average exterior chain length ($\overline{ECL}$) and average interior chain length ($\overline{ICL}$) of amylopectin from KSS7 starch are all higher than those from TNu67 and TCW70. The gel permeation chromatograph of KSS7 amylopectin, which is of lower DP_n, shows less amount of short chain fraction, but with a small amount of extralong chain fraction. And, no extralong chain fraction is detected in the other two amylopectins. Consequently, KSS7 amylopectin displays a higher degree of β-amylolysis and λ_{max} than the other two.

Dynamic rheological studies on starch gelatinization mechanism

Figure 1 displays the changes of the storage moduli (G') of KSS7 and TNu67 starches during heating at a rate of 1°C/min [8]. The temperature at which G' increases drastically and instantaneously is designated as $T_{G'}$ [8]. The increments of starch concentrations from 5 to 30 % can increase the gradient of G' notably and the value of maximum G' (G'_{max}), but with a lower $T_{G'}$. Both G' and $T_{G'}$ of TNu67 are higher than those of KSS7 at same starch concentration. The value of G' for TCW70 is very small, even with concentration up to 30 %. The results coincided with the fact that starch granule with low amylose content is less rigid and tended to disintegrate easily when swollen intensely and overcrowded [50].

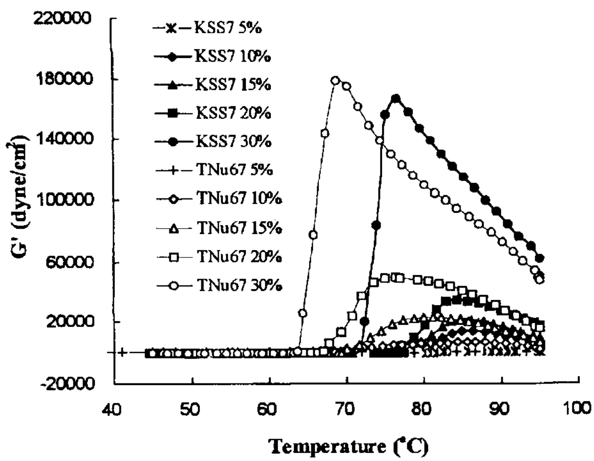

Fig. 1. Storage modulus (G') measurements of KSS7 and TNu67 at different concentrations during heating (frequency, 1Hz; strain, 0.015; heating rate, 1°C/min) [8].

The developments of loss modulus (G'') for these rice starch dispersions at different concentrations with elevating temperature are displayed in Figure 2 [8]. The influence of temperature on G'' of the rice starch is similar to that on G' (Fig. 1).

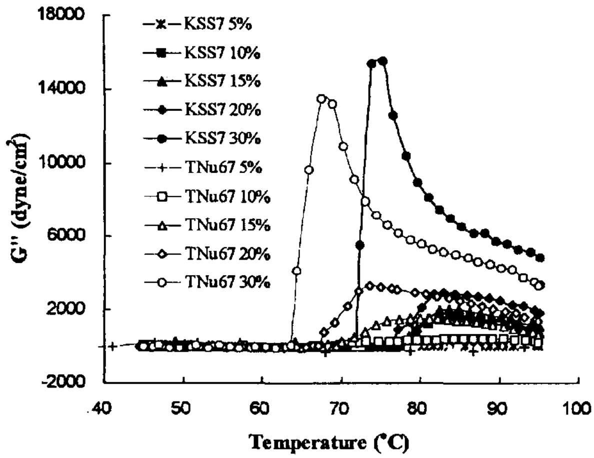

Fig. 2. Loss modulus (G'') measurements of KSS7 and TNu67 at different concentrations during heating (frequency, 1Hz; strain, 0.015; heating rate, 1°C/min) [8].

For further elucidating the heating behaviour of starch, some indices from Figure 1, including $T_{G'}$, $T_{G'max}$ (temperature at G'_{max}), $(dG'/dT)_{max}$ (the maximum slope of increasing G' against temperature), G'_{max} (maximum G'), G'_{95} (G' at 95°C) and $\tan\delta_{95}$ (ratio of G'' to G' at 95°C) are applied and listed in Table 3. While the concentration increasing from 10 % to 30 %, the values of $T_{G'}$ for KSS7 and TNu67 decrease from 78.7 to 72.4°C and 69.9 to 64.4°C; and $T_{G'max}$, from 86.4 to 76.6 and 85.6 to 68.8°C, respectively. The $(dG'/dT)_{max}$ of KSS7 and TNu67 raise with the increment of starch concentration up to the temperature of G'_{max} ($T_{G'max}$). The G' on continuous heating after $T_{G'max}$ will decrease to a certain level, depending on starch variety. The loss tangent (tanδ), which is an index of viscoelastic property, of KSS7 and TNu67 at 95°C reduce from 0.28 to 0.08 and 0.10 to 0.07, with the increase of concentration. These results indicate that TNu67 shows higher G'_{max}, lower G'_{95}, and more elastic than KSS7 during heating. The G'_{95} of 30 % TCW70 is only 950 dyne/cm^2. However, the value of tanδ (~0.4) implies that TCW70 in the concentration of 20–30 % tends to be elastic, or solid property, rather than liquid property.

Heating above $T_{G'}$ will promote the interactions between swollen granules and/or leached-out amylose and granule. Finally, G' reaches a maximum value (G'_{max}). After that, further heating provides the energy to breakdown the residual crystalline structure of the granule accompanying with releasing amylose [6, 8], and to enhance Brownian mobility. Consequently, swollen granules become softer and G' drops down. Keetels and Vliet (1994) [6] suggested that the initial increase of the G' could attribute to the degree of granule swelling just to fill the whole available volume of the system. And G'_{max} has been considered as one of the rheological parameters of swollen granule tightly packed.

Figure 3 demonstrates the concentration dependences of $T_{G'}$, $T_{G'max}$, $(dG'/dT)_{max}$ and G'_{max} for KSS7 and TNu67 starches. There is a linear logarithmic relation between $(dG'/dT)_{max}$ or G'_{max} and starch concentration, especially for TNu67. For KSS7, $(dG'/dT)_{max}$ or G'_{max} can be detected at concentration as low as 5 %. The $(dG'/dT)_{max}$ of KSS7 is in proportion to ($\propto$) $C^{3.90}$, and is close to that of TNu67 ($C^{3.95}$). However, the G'_{max} of KSS7 is $\propto C^{3.22}$, which exponent is larger than that of TNu67 ($C^{2.97}$). $T_{G'}$ of 10 % and 15 % KSS7 or TNu67 starches are similar to each other. Above 15 %, $T_{G'}$ decreases with the increment of concentration by the slopes of -0.419 (R^2 = 0.996) and -0.374 (R^2 = 0.994), respectively. This result implies that the temperature of the swollen granule just fulfilling the system will drop down with the increase of starch concentration at above 15 %. Whereas, the linear correlation be-

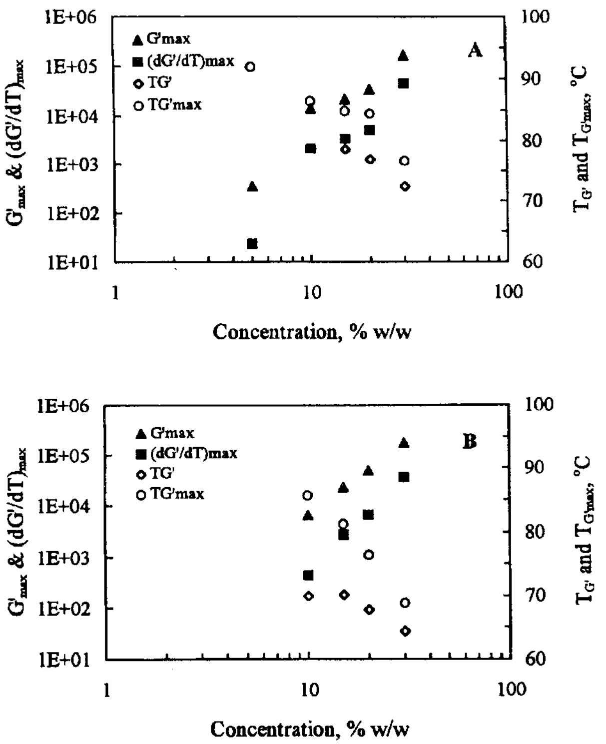

Fig. 3. Concentration dependences of rheological parameters and critical temperatures of KSS7 and TNu67 starches during heating (1°C/min) [51].

tween $T_{G'max}$ and concentration is observed with the gradient of -0.552 (R^2 = 0.935) for KSS7 or -0.841 (R^2 = 0.997) for TNu67. This suggests that the tight-packing temperature of swollen granule decreases with the reduction of moisture content.

Correlations between granular swelling and rheological properties of starch

The viscoelasticity of gelatinized starch dispersion is a result of a complicated combination of parameters involving the viscoelasticity of the continuous phase, the volume fraction of the dispersed phase, and the shape and deformability of the swollen particles [7]. Thus, it will be of great interest to learn the correlations between the dynamic rheological properties of starch dispersion and the swelling-solubility properties, degree of swelling, and the close-packing temperature of starch granule.

The swelling-solubility property of starch granule

The swelling-solubility properties, including swelling power, water soluble index (WSI), blue value and λ_{max}, of 1 % KSS7, TNu67 and TCW70 starch dispersions are shown in Figure 4 [51]. The changes in swelling power and WSI for these three starches suggests a two-stage process of swelling which fits the kinetics model mentioned by Kokini et al. (1992) [5]. The temperatures of first notable increase in swelling power are 65~75°C for KSS7 and 55~65°C for the other two (Figure 4A, C, E). The second stage of swelling drastically, accompanying with remarkable WSI increase, all occur at above 85°C. And this temperature is slightly higher than both T_c of gelatinization and $T_{G'max}$ in rheogram for 20 %. The degree of swelling power is TCW70 >> TNu67 > KSS7, where the swelling power of TCW70 is almost as high as two times of the other two. Both blue value and λ_{max} of KSS7 and TNu67 increase extensively at 65~75 and 55~65°C, respectively (Figure 4B&D). The changes in λ_{max} of KSS7 and TNu67 are from ~570 to ~630 nm with elevating temperature. As for TCW70, the blue value and λ_{max} increase slightly at above 75°C from ~0.0 to 0.1 and 520 to 570 nm, respectively (Figure 4F).

From the above results, the swelling for KSS7 and TCW70 starches in excess water are similar to the corn and tapioca starches, respectively [5], and the TNu67 behaves between them. These starches swell in different manners, reflecting varietal differences in the molecular organization within the granule. KSS7 granule is the most close-packed, and TCW70, the most unrestrained. This result is in accordance with the data of viscosity [45]. Generally, non-waxy starch (KSS7 or TNu67) has higher WSI and blue value than those of waxy starch (TCW70). It also indicates that the amount of water solubles of KSS7 at 95°C is much less than its amylose content (~25 %). That is, only one half of amylose molecules is leached out, and the residual amylose remains entangling with amylopectin within granule. Moreover, the amount of residual amylose within starch granule will increase with the increment of starch concentration [7, 15]. This entanglement (not crystallization) inside of the gelatinized KSS7 granule may be responsible for its higher G'_{95} than that of TNu67 (Table 3). Such phenomenon hints that the rigidity of swollen KSS7 granule can improve with the amylose fraction retaining within the granule.

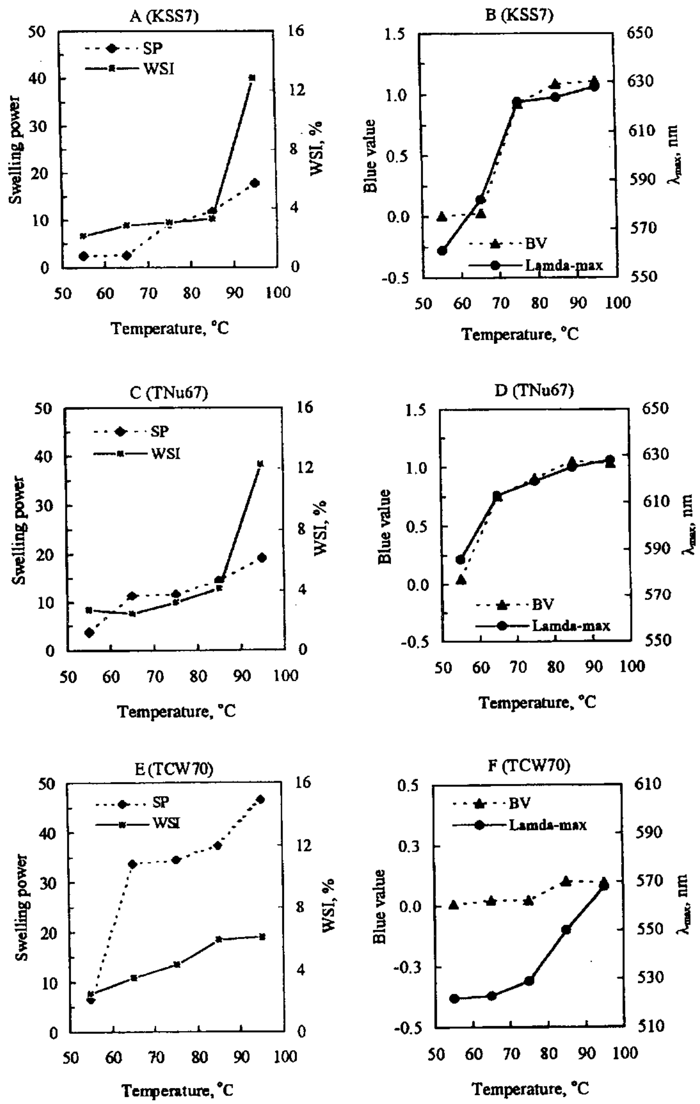

Fig. 4. The swelling power, WSI, blue value and λ_{max} as a function of temperature for 1 % (w/w) KSS7 (A, B), TNu67 (C, D) and TCW70 (E, F) starch dispersions [51].

Table 3

Effect of starch concentration on rheological properties of rice starches in water during heating [8]

Starch	Concn. %	$T_{G'}$ °C	$T_{G'max}$ °C	$(dG'/dT)_{max}$ dyne/cm^2·°C	G'_{max} dyne/cm^2	G'_{95} dyne/cm^2	$\tan\delta_{95}$
Indica- KSS7	5	nd [a]	91.9	22.9	346	182	0.28
	10	78.7	86.4	2135	14230	1619	0.17
	15	78.6	84.8	3436	21800	5746	0.12
	20	76.9	84.4	5144	34630	19680	0.11
	30	72.4	76.6	44736	167300	54760	0.08
Japonica-TNu67	5	nd	nd	nd	nd	479	nd
	10	69.9	85.6	439	6630	1651	0.10
	15	70.1	81.2	2759	23100	6486	0.09
	20	67.8	76.4	6584	49520	14970	0.09
	30	64.4	68.8	36006	178500	47150	0.07
Waxy--TCW70	5	nd	nd	nd	nd	nd	nd
	10	nd	nd	nd	nd	nd	nd
	15	nd	nd	nd	nd	nd	nd
	20	nd	nd	nd	nd	391	0.40
	30	nd	nd	nd	nd	950	0.39

[a] not detectable

For understanding the influence of WSI on the rheological properties of starch, it is important to clarify what molecular characteristics of the water soluble fraction is. Hizukuri [52] has demonstrated that the $\overline{CL}$ of water-soluble amylose is increased with elevating extraction temperature from 60–80°C. It may contribute the higher λ_{max} with higher temperature until granule breakdown during heating. The studies on 14 rice amylopectins by Chen [45] further prove such phenomenon. A linear relationship between averaged chain length ($\overline{CL}$) and λ_{max} (nm) for indica amylopectin is $\overline{CL} = 0.063(\lambda_{max}) - 16.845$ ($R^2 = 0.955$) (Figure 5A). And the ratio of extralong (a) and long (b) to short chains (c) is also in proportion to the λ_{max} for all 14 amylopectins and can be expressed by the equation of $(a+b)/c = 0.002\ (\lambda_{max}) - 0.575$ ($R^2 = 0.909$) (Figure 5B). Hence, it may conclude that the higher the λ_{max}, the greater is the $\overline{CL}$ of the leached-out molecules.

The λ_{max} of amyloses from KSS7 (DP_n=1075), TNu67 (DP_n=1004), wheat (Dp_n = 500~790) and potato (Dp_n = 4360~6990) starches are 650, 653, 645 and 665~670 nm, respectively; and λ_{max} of amylopectins are 579 nm for KSS7, 537 nm, TNu67, and 534 nm for waxy rice [52, 53]. Hence, the values of λ_{max} for three gelatinized starch dispersions shown in Figure 4 reveal that the average molecular sizes of leached-out matter are small for TCW70 and intermediate for KSS7 and TNu67. These swelling-solubility properties and the swollen granular structure are responsible for the dynamic rheological characteristics during gelatinization.

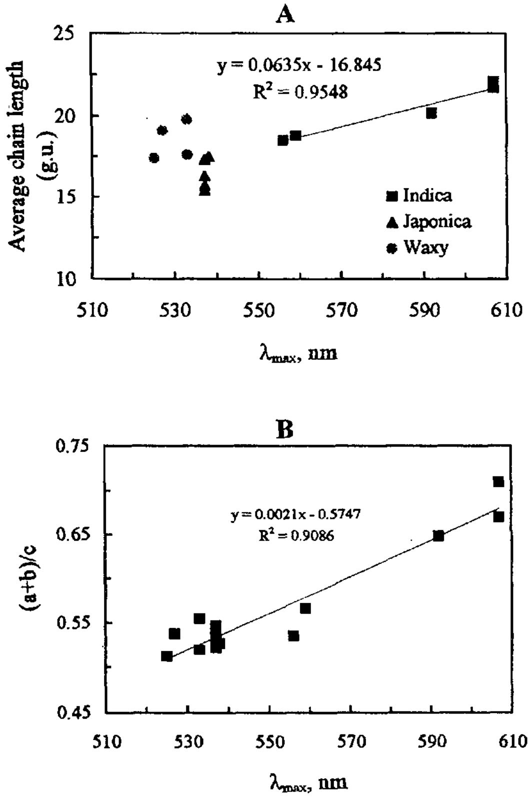

Fig. 5. Correlations between the average chain length (A) as well as extralong (a) + long chains(b)/short chain (c) (B) and λ_{max} for 14 rice amylopectins [45].

Contribution of the rigidity of swollen granule to dynamic rheological property of starch

Doublier, Ring and their co-workers [7, 15] have proposed that the rigidity of swollen granule can govern the rheological property of concentrated starch system, and the degree of influence is increased significantly with the increment of concentration. The rigidity of swollen granule can be simply estimated by the inverse of swelling value [7, 19]. The effects of the degree of granular swelling and the amount of leaching-out material on dynamic rheological properties have been conducted by heating the 20 % KSS7 dispersion up to 70~95°C, followed by cooling to 25°C. The rheological parameters including G'_{T_f} (G' at final heating temperature T_f), tan δ_{Tf} (tanδ at T_f) on heating, and the $(dG'/dT)_{max}$ (maximum slope of G' increase), G'_{25} (G' at 25°C), tan δ_{25} (tanδ at 25°C) as well as G'_{25}/G'_{T_f} during cooling are listed in Table 4 [8]. The $(dG'/dT)_{max}$ or G'_{25}/G'_{T_f} can be applied as a retrogradation index. No modulus development is observed while the starch dispersion is heated up to 70°C (Table 4). When the temperature is raised up to 75°C (near to the Tp of gelatinization), a negligible G'_{75} shows on rheogram, but with a significant G' development on cooling. It leads to a high G'_{25}/G'_{75} ratio, 16. When the starch dispersion is cooked up to 80 or 85°C (higher than the Tp of gelatinization), the respective G'_{80} (40710 dyne/cm^2) and G'_{85} (41660 dyne/cm^2) are higher than the other temperatures. Consequently, high $(dG'/dT)_{max}$ and G'_{25} on cooling are obtained. Heating at 85°C can result in the starch system of the highest G'_{Tf} , G'_{25}, $(dG'/dT)_{max}$, elasticity (i.e. lowest tanδ) and G' declines at the late stage of cooling among the heating-cooling processes examined. Above 85°C (higher than T_c of gelatinization), elevating temperature will decrease G'_{Tf}, $(dG'/dT)_{max}$, and G'_{25}. However, tanδ reduces from 0.08~0.11 to 0.03.

Table 4

Effect of final heating temperature on rheological properties of 20 % KSS7 sratch [8]

Final Heating Temperature T_f, (°C)	Heating G'_{Tf} (dyne/cm^2)	Heating $\tan\delta_{Tf}$	Cooling $(dG'/dT)_{max}$ (dyne/cm^2·°C)	Cooling G'_{25} (dyne/cm^2)	Cooling $\tan\delta_{25}$	G'_{25}/G'_{Tf}
70	nd[a]	nd	nd	nd	nd	nd
75	74	0.48	22	1186	0.39	16.0
80	40710	0.08	458	65890	0.03	1.6 [b]
85	41660	0.08	504	71880	0.03	1.7 [b]
90	31770	0.09	490	63630	0.03	2.0
95	17320	0.11	395	45010	0.03	2.6

[a] not dectectable
[b] G' drops at the late stage of cooling

From the data of Figure 4 and Table 4, the starch heated up to 70°C does not show any notable modulus is due to not gelatinized yet. High G'_{25}/G'_{75} ratio for the 75°C is the result of interaction between partially gelatinized, moderately swollen granule and a fairly small amount of shorter-chain solubilized material. The granule of 85°C with an appropriate degree of swelling and some residual crystallites, and a small amount of longer-chain solubles are responsible for the maximal G'_{Tf} , $(dG'/dT)_{max}$ and G'_{25}. Above 90°C, the melting of remaining crystallites inside granule and most amylose releasing from granule cause the swollen granules to become softer. This softening of swollen granule should be the reasons of low modulus and $(dG'/dT)_{max}$. Furthermore, a large amount of long-chain amylose leaching-out into solution at 90~95°C (Figure 4A) tends to improve the G'_{25}/G'_{95} on cooling (Table 4). The importance of rigidity of swollen granule on the dynamic rheological properties is also shown for concentrated starch system [6, 15].

Relations between the temperatures of granular close-packing and G' increase

Bagley & Christianson (1982) [19] have introduced the product of granular swelling capacity (Q) and starch concentration (C) in a suspension free of solubilized material as a true measurement of whether there is excess water between the swollen granules (CQ < 1) or not (CQ > 1). When excess solvent is present, CQ is less than unity and is equivalent to the volume fraction (ϕ) of swollen granule in the system. CQ can be greater than unity for deformable granules. Taking into account that part of starch is solubilized, Doublier et al. (1987) [7] have further expressed the relationship among the volume fraction of the swollen granule (ϕ), concentration, swelling power and solubility as the following equation:

$$\phi = C \cdot Q \cdot (1 - S/100) \qquad (1)$$

Where C is starch concentration expressed in g/g; Q, swelling power in g/g; and S, WSI in %. When $\phi < 1.0$, the swollen granules are dispersed in excess water, and $\phi = 1.0$, the swollen granules just fill up starch system [7, 19, 21]. The temperature at which the swollen granules just fill up the system is designated as $T_{\phi=1}$ [22].

The mass fraction (ϕ) of starch granule at a certain concentration and temperature can be calculated from equation (1) by introducing the values of swelling power and WSI. $T_{\phi=1}$ for a known concentration can be derived by interpolation method from plot of ϕ *versus* temperature. The relations between the T_G' in rheogram and $T_{\phi=1}$ for 5~40 % KSS7 concentrations are displayed in Figure 6 [51]. Both T_G' and $T_{\phi=1}$ decrease with the starch concentration increases. There are two concentration

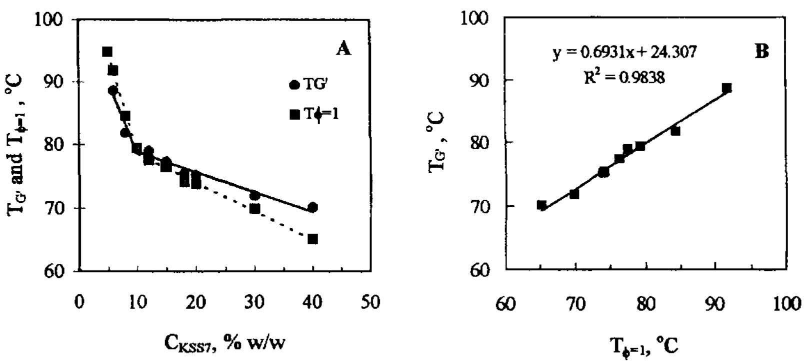

Fig. 6. Concentration dependences (A) and correlation (B) of the critical temperatures T_G' and $T_{\phi=1}$ of KSS7 starch [51].

dependences of $T_{G'}$ or $T_{\phi=1}$ for KSS7 starch dispersions with a turning point at 10 % concentration. Below 10 %, $T_{\phi=1}$ is higher than $T_{G'}$; and above, $T_{\phi=1}$ is lower than $T_{G'}$. This result reveals that the restricted swelling of starch granule occurs at above 10 %, which is also in accordance with the data of Figure 3. $T_{G'}$ and $T_{\phi=1}$ should be identical, if the initial increase in storage modulus is contributed by the swelling of starch granules to occupy the available volume of the system as proposed by Keetels and Vliet [6]. The discrepancy between $T_{\phi=1}$ and $T_{G'}$ may be due to the influence of the starch concentration on Q and S in eq (1).

It has been manifested swelling power and WSI will decrease with the increment of concentration [7, 15]. Nevertheless, the degrees of influence from swelling power and WSI on rheological properties of starch system may vary with different concentrations. The granule of 5 to 10 % concentration may swell as freely as that of 1 % before close packing, because of still excess water in the system. Consequently, Q value should not be affected by the concentration. One can attribute the high $T_{\phi=1}$ to over-estimate of S value applied in the eq (1) under these low concentration systems. At concentration higher than 10 %, both $T_{G'}$ and $T_{\phi=1}$ are lower than 80°C. The value of WSI (S) is very small. The result of low $T_{\phi=1}$ from over-estimate of Q value is anticipated.

At low concentration (< 10 %), generally, the value of WSI should be considered for interpreting the pasting behaviour of starch system; and at high concentration (> 10 %) the swelling power should be taken into account. In addition, measurements of both $T_{G'}$ and $T_{\phi=1}$ may be affected by the rigidity of swollen starch granule, although such influence is difficult to prove. It is interesting to point out that a linear relation between $T_{G'}$ and $T_{\phi=1}$ of KSS7 is detected, irrespective of starch concentration. The relationship can be expressed as the equation of $T_{G'} = 0.69T_{\phi=1} + 24.31$ ($R^2 = 0.984$) (Figure 6B).

Rheological characteristics of starch during retrogradation

During cooling, the G' for gelatinized KSS7 and TNu67 starches at different concentrations increase steadily with decreasing temperature as shown in Figure 7 [8]. The increments of slope of G' against cooling temperature for the two starches are in proportion to the concentration. And KSS7 exhibits higher slope and G' than those of TNu67. The decline of G' for 30 % starch dispersions may be due to rapid cooling during the measurement. However, further investigation is required for the elucidation of such peculiar phenomenon.

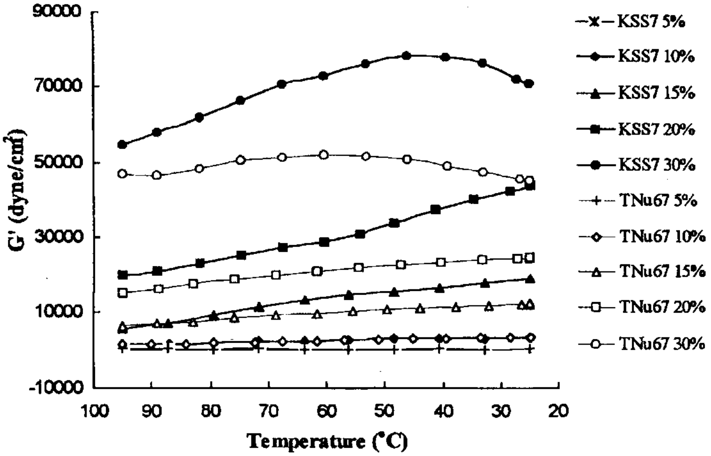

Fig. 7. Storage modulus (G') measurements of KSS7 and TNu67 starches at different concentrations during cooling (5°C/min) [8].

$(dG'/dT)_c$ (gradient of raising G' during cooling), G'_{25} (G' at 25°C), $\tan\delta_{25}$ ($\tan\delta$ at 25°C), and G'_{25}/G'_{95} of KSS7, TNu67 and TCW starches are applied for the indices of rheological properties during retrogradation. At low concentration (5~10 %), the gelatinized TNu67 shows higher $(dG'/dT)_c$ and G'_{25}, but lower $\tan\delta$ than those of KSS7 and TCW70. However, at high concentration (15~30 %), $(dG'/dT)_c$ of KSS7 (193~499 dyne/cm^2·°C) is at least as high as two times of TNu67 (81~139 dyne/cm^2·°C). Consequently, the G'_{25} of KSS7 (19060~68200 dyne/cm^2) is significantly greater than that of TNu67 (12380~45720 dyne/cm^2). TCW70 exhibits very slow rate of retrogradation and low G'_{25} (442~1107 dyne/cm^2 for 15~30 %). The values of $\tan\delta_{25}$ for 15~30 % starch concentrations of KSS7, TNu67 and TCW70 are 0.03~0.04, 0.05~0.06 and 0.39~0.54, respectively. These data indicate that the elasticity of retrograded starch dispersion is KSS7 > TNu67 >> TCW70.

The concentration dependences of $(dG'/dT)_c$ and G'_{25} for the three starches follow power laws as depicted in Figure 8 [51]. The result of regression analysis indicates that $(dG'/dT)_c$ of KSS7 is in proportion to $C^{3.9}$ ($R^2 = 0.927$), which exponent is close to that of TNu67 ($C^{3.9}$) ($R^2 = 0.996$). And, G'_{25} of KSS7 increases linearly with $C^{3.2}$ ($R^2 = 0.968$), which exponent is much larger than that of TNu67 ($\propto C^{2.4}$) ($R^2 = 0.970$). As for TCW 70, the G'_{25} is in proportion to $C^{1.4}$ ($R^2 = 0.920$) [8]. The concentration dependence of TCW70 paste is very similar to that of 4.2~16.7 % potato starch ($C^{1.5}$) [40], implying both starches have resembling pasting behaviours. Biliaderis and Juliano [38] reported that the moduli of rice starches are related with $C^{2.2\sim2.9}$

And, the dependence of moduli for 1.5~7.0 % amylose gels is $C^{3.1}$ [54] or $C^{7.0}$ [55]. Thus, the exponent value for starch dispersion may depend on the chain size distributions of amylose and amylopectin, the integrity as well as rigidity of swollen granule [7], and the range of polymer concentration measured, gel preparation [54], and measurement conditions, etc. The low concentration dependence of modulus for polysaccharide system has been considered as a result of high degree of polymer network defect due to the extensive entanglement among molecular chains [56].

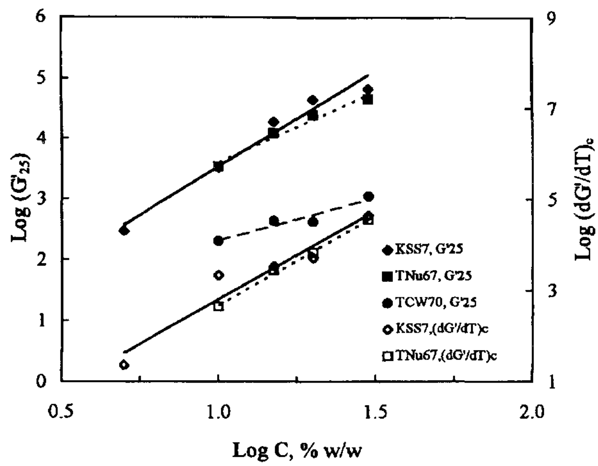

Fig. 8. The storage modulus (G') and $(dG'/dT)_c$ of different rice starches as a function of concentration during cooling [51].

The cold starch gel is more rigid than the hot starch gel [57], and KSS7 or TNu67 starch gel can be developed at heating stage for a starch system with an enough concentration. The G' increases during cooling, may be driven by the interactions, including hydrogen-bond formation favored at lower temperatures (exothermic), of starch constituents [8, 10, 11, 39, 54]. It mainly due to the retrogradation of amylose in short period [3, 10, 11, 15, 33, 54, 58]. The facts that KSS7 gel with higher G' than TNu67 during cooling, and TCW70 only makes a paste may attribute to the differences in amylose/amylopectin composition and fine structure of amylopectin in the swollen granule [54]. It has been found that the cereal amylopectins have a reduced rate of retrogradation due to their shorter average chain-length [24]. Similar results were also found in the studies of 14 rice amylopectins [45].

Frequency dependence of rheological properties for starch gel and paste

The effects of frequency from 0.01 to 20 Hz on the values of G' for 20 % KSS7 and TNu67 at 25°C during measurements are little and similar (Figure 9A) [51]. But the G' of TCW70 gains drastically with the raise of frequency at above 5 Hz. And the frequency dependence of G'' is KSS7 < TNu67 < TCW70 (Figure 9B). Due to the G''/G, ratio is of the order of 0.01~0.1 and the variation in G, with frequency is small, the 20 % KSS7 and TNu67 can be considered as "true gel" [8, 51, 59]. And, 20 % TCW70 exhibits a very weak gel with a G''/G' > 0.1, resembling a concentrated entangled solution as described by Morris and Ross-Murphy (60); and can be classified into "pseudo gel" [59] or "paste" [8].

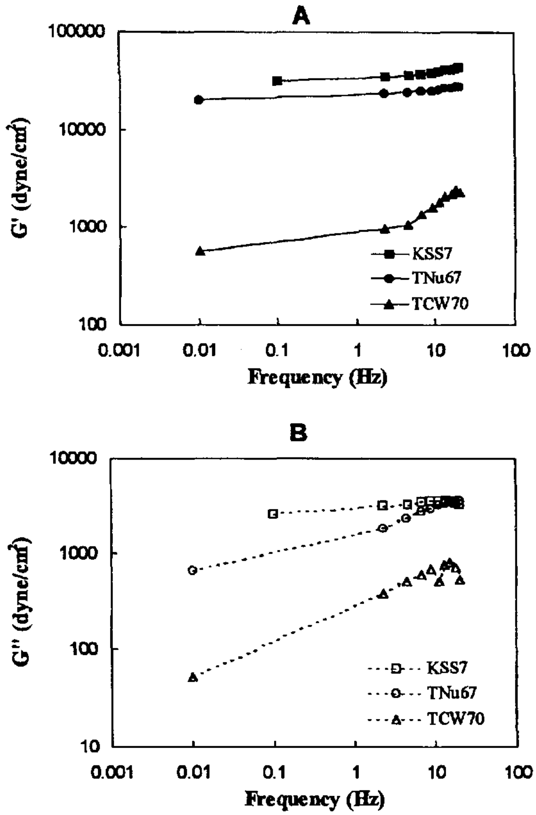

Fig. 9. Frequency dependence of 20 % (w/w) KSS7, TNu67 and TCW70 rice starches at 25°C. (samples prepared by heating up to 95°C (1°C/min) and then cooling down to 25°C (5°C/min); strain, 0.015) [51].

Influence of heating rate on the rheological properties of starch dispersion

Lower heating/cooling rate applied for the 20 % KSS7 starch dispersion can give higher G'_{95} and G'_{25} of the resulting gel (Table 5) [8] due to providing enough time for the granule swelling, the amylose leaching-out, and enhancing the interactions among amyloses and swollen granules. The starch treated by a heating-cooling rate of 2°C/min has a lower G'_{95} than that of 1°C/min, but both values of G'_{25} are similar after cooling. However, high G'_{25}/G'_{95} ratio, one of retrogradation indices, is observed for fast heating/cooling rate. One may ascribe this high ratio to the rigidity of swollen granule because of restricted swelling. Moreover, it is possible that quick cooling causes "immobilization" of chains in the gel network and, consequently, low modulus values [54].

Table 5

Effect of heating/ cooling rate on rheological properties of 20 % KSS7 gel at 95°C and 25°C [8]

Heating/Cooling Rate (°C/min)	Up to 95 °C G'_{95} (dyne/cm²)	$\tan\delta_{95}$	Down to 25 °C G'_{25} (dyne/cm²)	$\tan\delta_{25}$	G'_{25}/G'_{95}
1	17320	0.11	45010	0.03	2.60
2	13660	0.12	45640	0.03	3.34
5	9697	0.14	38350	0.03	3.95

Interactions between amylose and starch granule

Since the content and average chain length of solubilized amylose, the content and fine structure of amylopectin, granular rigidity and swelling capacity, all can influence the rheological properties of starch dispersion during gelatinization and retrogradation. The effect of addition of amylose or amylopectin, as well as mixing starches on the rheological behaviour of starch during heating are investigated in order to illustrate the interaction mechanisms among them.

Mixed starch system – KSS7/TCW70

During Heating

The rheological properties of the mixed starch samples with different ratios of KSS7 and TCW70 during heating are shown in Figure 10 [22]. The figure shows that 20 % KSS7 starch system gives the highest G', and 20 % TCW the lowest. A peculiar phenomenon is also detected from the figure. Although the total starch concentration of the mixture of 15 % KSS7 and 5 % TCW70 sample was higher than that of 15 % KSS7 alone, the G' of the former is smaller than the latter during heating.

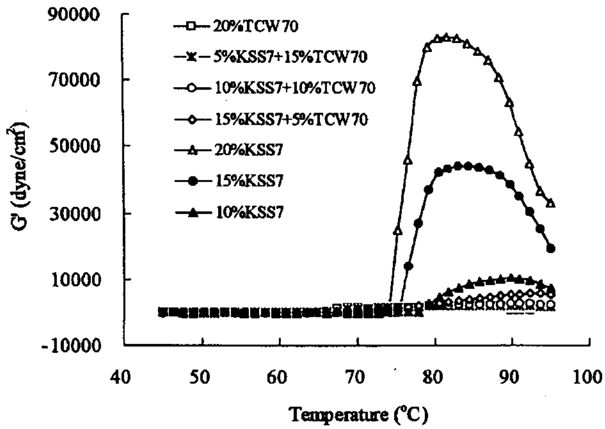

Fig. 10. Storage modulus (G') measurement of mixed KSS7/TCW70 starch systems at different ratios (frequency, 1 Hz; strain, 0.015; and heating rate, 1°C/min) [22].

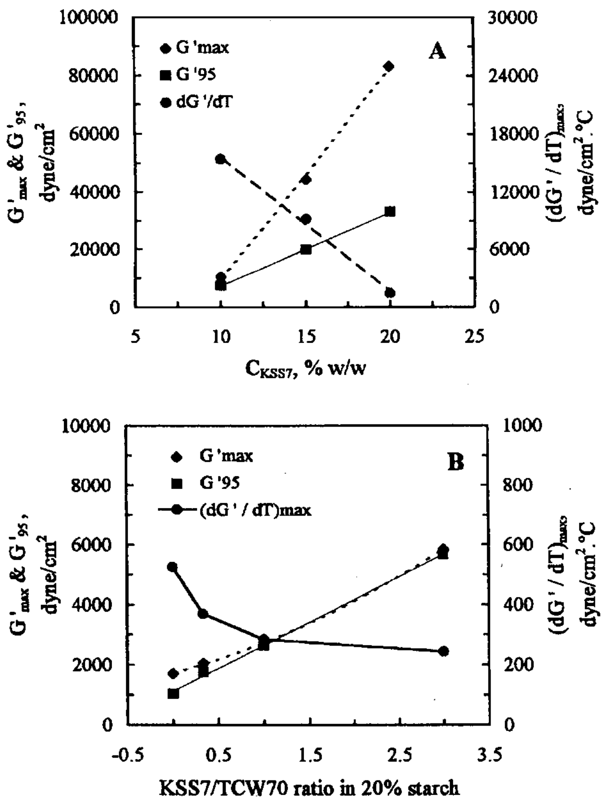

Fig. 11. G' and $(dG'/dT)_{max}$ of KSS7 at different concentrations (A) and of mixed KSS7/TCW70 at different ratios (B) during heating [51].

The rheological characteristics between KSS7 alone and KSS7/TCW70 mixed systems are varied significantly. G'_{max} and G'_{95} of KSS7 alone are in proportion to the starch concentration (C_{KSS7}) (Figure 11A). The effect of concentration on G'_{max} is much higher than on G'_{95}. And, $(dG'/dT)_{max}$ (the maximum slope of G' vs. T) of KSS7 starch is in inverse proportion to C_{KSS7} linearly. For KSS7/TCW70 mixed system (Figure 11B), both G'_{max} and G'_{95} value are relatively low and very close when the ratio of KSS7 to TCW70 ≥ 1. And higher proportion of KSS7 in the starch mixture will affect the dG'/dT more.

The concentration dependences of $T_{G'}$ and $T_{G'max}$ for mixed KSS7/TCW70 are also different from those of KSS7 alone (Figure 12). Both $T_{G'}$ and $T_{G'max}$ for KSS7 alone can be presented as a linear function of its concentration (C_{KSS7}) (Figure 12A); $T_{G'} = -0.4C_{KSS7} + 82.8$ ($R^2 = 0.893$), and $T_{G'max} = -0.76C_{KSS7} + 96.8$ ($R^2 = 0.951$). However, both $T_{G'}$ and $T_{G'max}$ for KSS7/TCW70 mixture increase nonlinearly with the raising ratio of KSS7/TCW70

(Figure 12B). $T_{G'}$ for all mixed ratios are in the range of 65 to 70 °C and much lower than those of 10~20 % KSS7 alone. And $T_{G'max}$ of mixture increases exponentially with the increment of KSS7/TCW70 ratio. $T_{G'max}$ of mixed 10 % each of KSS7 and TCW70 system is similar to that of the 10 % KSS7 alone. Moreover, $T_{G'max}$ of KSS7/TCW70 ratio < 1 is lower, but >1 is higher, than that of KSS7 alone at same C_{KSS7}. Generally, $T_{G'max}$ is more feasible to be affected by starch concentration or the ratio of mixture than $T_{G'}$.

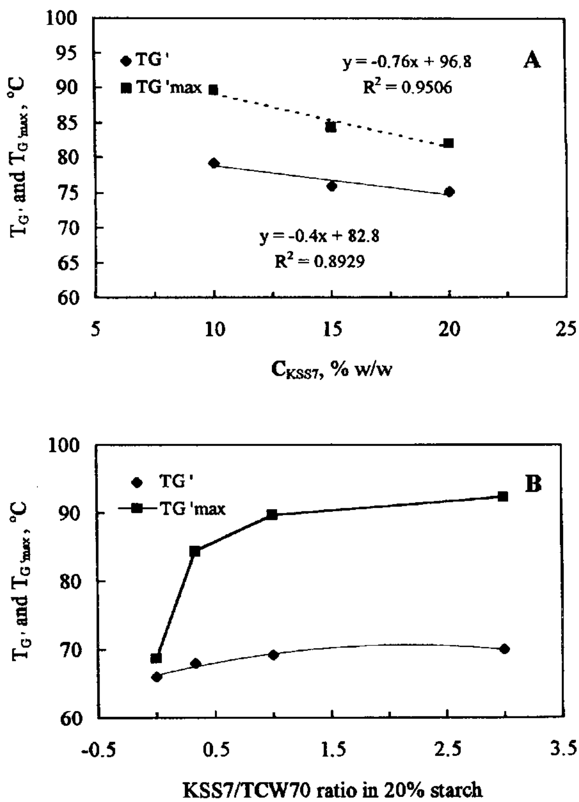

Fig. 12. $T_{G'}$ and $T_{G'max}$ of KSS7 at different concentrations (A) and of mixed KSS7/TCW70 at different ratios (B) during heating [51].

Because that neither significant modulus (G'_{max} or G'_{95}) nor $T_{G'}$ or $T_{G'max}$ is developed in TCW70 even up to 30 % concentration during heating, the rheological properties of the KSS7-TCW70 mixture (Figure 11 & 12) may attribute mainly to the heating behaviours of KSS7 starch with the influence of swollen TCW70. This influence may come from two actions. First, TCW70 starch granule swells much earlier and binds higher amount of water than does KSS7. Consequently, it retards the swelling of granule and leaching-out of amylose for KSS7. Secondly, the unswollen KSS7 granule may be excluded by the swollen TCW70 granule, resulting in a phase-separated mixed gel of very low moduli. These phenomena are resembling that the addition of amylopectin will restrict starch granules from swelling as suggested by Svegmark et al.[39].

<u>During Cooling</u>

Figure 13 shows the change of G' for KSS7/TCW70 mixed system during cooling [22]. The gradient of G' against temperature in KSS7 alone as well as the mixed

KSS7/TCW70 increases with the increment of C_{KSS7}. The dependences of G'_5 and $(dG'/dT)_{max}$ on starch concentration for both systems are exhibited in Figure 14. G'_5 and $(dG'/dT)_{max}$ as a function of C_{KSS7} for KSS7 system alone can be expressed as: $G'_5 = 5374\ C_{KSS7} - 40353$ ($R^2 = 0.994$) and $(dG'/dT)_{max} = 61\ C_{KSS7} - 552$ ($R^2 = 1.000$) (Figure 14A). As for the KSS7/ TCW70 mixed system, equations are $G'_5 = 3309\ R_{KSS/Tcw} + 1144$ ($R^2 = 1.000$) and $(dG'/dT)_{max} = 23.3\ R_{KSS/Tcw} - 1.45$ ($R^2 = 0.999$) ($R_{KSS/Tcw}$, the concentration ratio of KSS7 to TCW70 in 20% starch) (Figure 14B). The results demonstrate that G' decreases profoundly in the mixed system, but linear relationship between the G' or $(dG'/dT)_{max}$ and C_{KSS7} still exists.

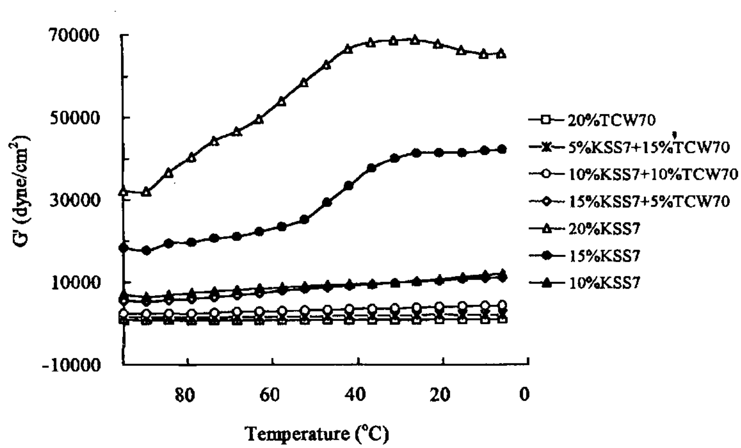

Fig. 13. Storage modulus (G') measurements of mixed KSS7/TCW70 starch systems during cooling (5°C/min) [22].

The 15 % KSS7 alone shows the highest G'_5/G'_{95} among all KSS7 and KSS7/TCW70 systems measured (Figure 15A) [51]. For the mixed KSS7/TCW70, G'_5/G'_{95} increases steadily with elevating C_{KSS7} (5~15 %) (Figure 15B). And those of 10 % KSS7 alone and 10 % each of KSS7/TCW70 are similar to each other.

Addition of KSS7 amylose

On KSS7 starch

The effects of added amylose on the rheological properties of KSS7 starch during heating, cooling and aging stages are listed in Table 6 [22]. Where the DP_n of isolated amylose is about 1000 (Table 1). Generally, Table 6 shows that those with addition of 2% amylose gives lower G'_{95}, but similar G'_5, and higher G'_{5A} (aging at 5°C for 1 h), except for the 20 % KSS7+2 % AM system. The G'_5 and G'_{5A} of the 20 % KSS7+2 % AM are slightly lower than those of 20 % KSS7 alone, reflecting an effect presumably via the competition of added amylose for water against the starch. Moreover, the values of $\tan\delta_5$ and $\tan\delta_{5A}$ for added amylose systems are higher than those of KSS7 alone. This result suggests that a phase separation may occur in this gelatinized mixture as examined by the TEM of amylose/potato starch system [39]. However, the degree of incompatibility between KSS7 starch and amylose is far less than that of KSS7 and TCW70 starches (Figure 14).

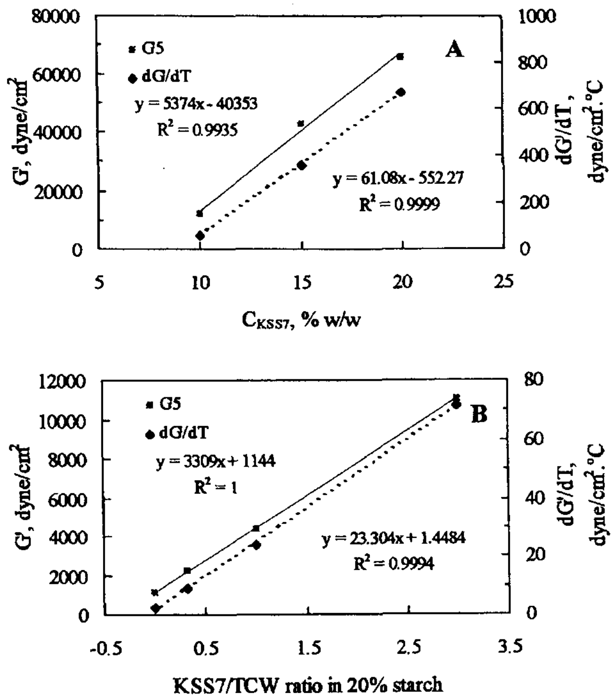

Fig. 14. G' and dG'/dT of KSS7 at different concentrations (A) and of mixed KSS7/TCW70 at different ratios (B) during cooling [51].

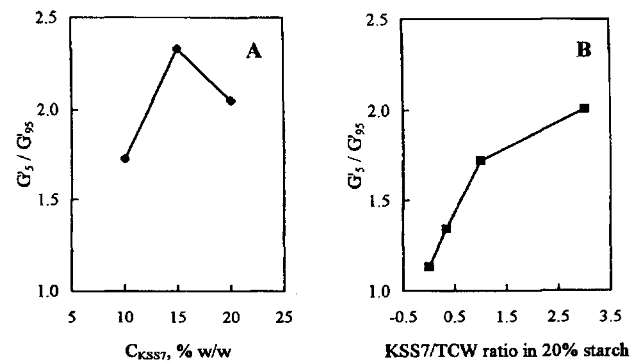

Fig. 15. Values of G'_5/G'_{95} of KSS7 at different concentrationd (A) and of mixed KSS7/TCW70 at different ratios (B) during heating-cooling cycle [51].

Table 6

Effect of added amylose on the rheological properties of KSS7 dispersions during heating, retrogradation and aging [22]

	Heated to 95 °C		Cooled to 5 °C		Aging at 5 °C for 1 hr	
	G'_{95} [a]	tan δ_{95}	G'_5	tan δ_5	G'_{5A}	tan δ_{5A}
5% KSS7	507±8 [b]	0.10±0.00	563±12	0.06±0.00	578±24	0.11±0.01
5% KSS7 +2% AM [c]	188±5	0.18±0.01	557±10	0.14±0.02	1710±283	0.06±0.00
10% KSS7	6995±190	0.08±0.00	12730±156	0.04±0.00	17120±230	0.03±0.00
10% KSS7 +2% AM [c]	4072±269	0.10±0.02	12730±2140	0.05±0.00	19050±1715	0.04±0.00
20% KSS7	32210±645	0.07±0.00	65960±255	0.04±0.00	66290±270	0.03±0.00
20% KSS7 +2% AM [c]	33450±2311	0.07±0.00	60530±2185	0.04±0.00	61250±2267	0.04±0.00

[a] G' (dyne/cm^2).
[b] Mean ± standard deviation. n = 3.
[c] 2 % KSS7 amylose added.

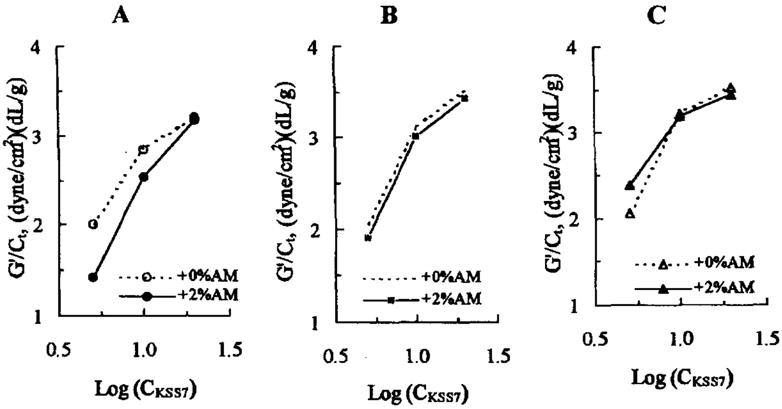

Fig. 16. Effect of added amylose on the G'/C_t at 95°C (A), 5°C (B), and aged at 5°C for one hour (C) for KSS7 (C_t, the total starch concentration) [51].

The ratio of G' to total concentration of the whole starch system (C_t) can be applied to further illustrate the influence of added amylose on the rheological properties [51]. The G'/C_t at 95°C for the 5~15 % KSS7 alone are significantly higher than those with 2 % added amylose (Figure 16A). The higher the C_{KSS7}, the smaller is the difference in G'/C_t between the samples with and without addition of amylose. No significant difference of G'/C_t is detected while C_{KSS7} raises up to 20 %. Although the addition of amylose to the KSS7 starch at 5~15 % brings a lower G'/C_t at 95 °C, the similar value of G'/C_t is obtained when it is cooling down to 5°C (Figure 16B) or after aging (Figure 16C). 5 % KSS7+2 % AM demonstrating a higher G'/C_t after aging for one hour is an exception. The result imply that the enhancement of retrogradation is only found in the system with high ratio of added amylose to starch.

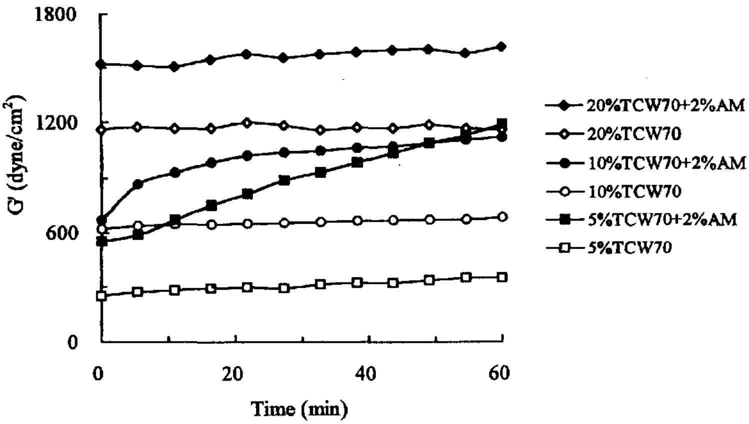

Fig. 17. Effect of added amylose on the time dependence of storage modulus (G') of TCW70 starch during aging at 5°C [22].

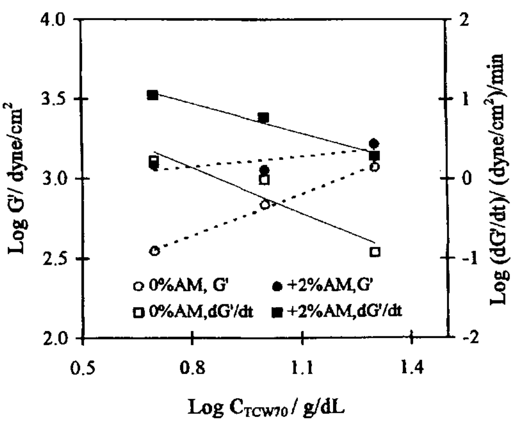

Fig. 18. Effect of added amylose on the concentration dependence of G' and dG'/dt for TCW70 starch during aging at 5°C [51].

On TCW starch

The influences of added amylose on the rheological properties of TCW70 paste can be observed in the stage of cooling and aging. The addition of 2 % amylose raises G' largely during cooling. Subsequently, it improves G' and dG'/dt (where t is the aging time, min) of aged sample (Figure 17 & 18), especially at concentration of 5 and 10 % [22]. This increment may attribute to the gelation of amylose [10, 11, 33]. However, the G' does not increase remarkably in the concentrated TCW70 system (20 %). Svegmark et al. (1993) [39] also indicated that 1–10 % potato starch swollen in the amylose solution exhibits a lower complex modulus (G^*) than the starch swollen in water during heating and a sharp increase in G^* is observed due to amylose gel formation during cooling.

Conclusion

The changes in rheological properties of starch dispersions during gelatinization and retrogradation controlled predominately either by the swelling-solubility properties or the interaction between starch constituents and water molecule can be identified. At low concentration (< 10 %), the rheological properties of starch dispersion during heating and cooling are governed mainly by the amount and chain length of water-soluble constituents. The significance of the granular characteristics such as the degrees of granular rigidity and close-packing, molecular sizes and distribution of amylopectin branches, and the presence of residual microcrystallite on the pasting behaviour is raising with increment of starch concentration. All these parameters can influence the concentration dependence of modulus for starch dispersion, and the formation of whether "gel" or "paste". Among the starches studied the KSS7 starch gel possessing the highest G' and dG'/dT in the heating-cooling cycle can attribute to the high ratio of extralong and long chains to short chain in amylopectin, the presence of soluble with longer chain length, the amount of unreleased amylose entangled within granule, and high rigidity of granule.

The effects of mixing different starches and the adding amylose into a system on shear modulus of the mixed dispersion depends on the swelling-solubility properties, and/or the composition and structure of starch granule. The addition of 2 % KSS7 amylose can decrease the modulus development of starch dispersion during heating, but improve significantly the modulus and retrogradation rate of KSS7 and TCW70 starches at a moderate concentration during cooling and aging. Further investigation is required to clarify the mechanisms of contributions from the degree of granular rigidity, the volume fractions and moduli of continuous and dispersed phases in the system, and amounts of amylose inside and outside of granule to the rheological properties of starch dispersion.

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BADANIA NAD KLEIKOWANIEM I RETROGRADACJĄ SKROBI ZA POMOCĄ REOMETRII DYNAMICZNEJ – WPŁYW STRUKTURY GAŁECZEK I SKŁADU

Streszczenie

Dokonano przeglądu badań nad kleikowaniem i retrogradacją skrobi za pomocą dynamicznej reometrii. Dyskusja dotyczy badań nad trzema odmianami skrobi ryżowej: indica (KSS7), japonica (Tnu67) i woskowej (TCW70). Zawierają one odpowiednio 24–26 %, 15–16 % i 0.8–1.0 % amylozy. Omówiono zachowanie się tych skrobi w czasie ogrzewania, chłodzenia i dodawania amylozy.

Do wyjaśnienia mechanizmu retrogradacji i kleikowania oraz zależności pomiędzy strukturą cząsteczkową skrobi i strukturą gałeczek skrobiowych posłużono się korelacjami pomiędzy pęcznieniem, rozpuszczalnością w wodzie, reakcją z jodem, temperaturą kleikowania i dynamicznymi reogramami. Na ogół wzrost G' w czasie kleikowania zależy od charakterystyki gałeczek, tj. sztywności pęczniejących gałeczek i oddziaływania między upakowanymi gałeczkami. Jednakże G' w retrogradacji skrobi zależy ponadto od oddziaływań między amylozą, która wypłynęła z pęczniejących gałeczek lub amylozy dodanej w trakcie doświadczeń i spęczniałymi gałeczkami. W przypadku układu mieszanego, np. skrobi woskowej z niewoskowymi G' drastycznie maleje. Dodatek amylozy wyraźnie obniża G' dla kleikowania, ale podwyższa G' w trakcie chłodzenia i starzenia. Dlatego wydaje się, że ziarnistość skrobi i charakterystyka gałeczek są głównymi czynnikami wpływającymi na reologiczne zachowanie się skrobi. Kolejnym istotnym czynnikiem jest amyloza wydobywająca się z gałeczek w czasie kleikowania, szczególnie w przypadku układów o dużym stężeniu.