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EFFECTS OF STARCH CHEMICAL STRUCTURES ON GELATINIZATION AND PASTING PROPERTIES

Abstract

Chemical structures, including amylose contents, amylopectin molecular sizes, branch chain lengths and distributions, and starch phosphate monoester and phospholipid contents, of a wide varieties of starches were analyzed. Thermal properties of starch gelatinization and retrogradation and starch pasting properties were also investigated. Results of the studies have shown that amylopectin branch chain lengths and their distributions govern the starch gelatinization temperature. Short average branch chain lengths and large proportions of short branch chains (DP11-16) relative to chains of DP 18-20 (a shoulder found in many starches) are likely to result in low gelatinization temperatures. Phosphate monoester derivatives also lower gelatinization temperature. With the same amylopectin structure, increasing amylose contents lower the starch gelatinization temperature. Methods of starch isolation also affect starch gelatinization temperature. Amylose contents significantly affect the pasting properties of starch. Normal cereal starches contain lipids and phospholipids, which display higher pasting temperatures, lower peak viscosity, and lower shear thinning than their waxy starch counterparts. Without lipids, normal potato starch displays a higher peak viscosity than waxy potato starch. Branch chain length of amylopectin also affects the pasting properties of starch. The presence of very long branch chains restrict starch swelling and increase the pasting temperature of starch and decrease the shear thinning. Phosphate monoester derivatives decrease the pasting temperature and enhance the viscosity by charge repelling. In contrast, phospholipids, by complexing with amylose and long branch chains of amylopectin, restrict the starch swelling and reduce the viscosity.

Introduction

Starches isolated from different sources are known to have different granule shapes, sizes, [1] chemical structures [2] and physical properties. Great research efforts have been devoted to reveal how the chemical structures affect the functional properties of starch. With advances in genetic engineering of starch structure modifications,

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there are increasing needs of understanding how the structures of starch should be changed to deliver desired properties for market needs.

The advances in analytical techniques have enabled us to elucidate the fine structures of starch and to gain additional knowledge of how chemical structures of starches govern the functional properties. In the past decade, my colleagues and I have focused our efforts on the study of starch structures and functional properties and to develop correlation between the two. In this lecture, I will report some results of our recent findings on amylose contents, amylopectin molecular sizes, branch chain lengths, distributions, and starch phosphate monoesters and phospholipids contents of a wide variety of starches and their effects on the gelatinization, retrogradation, and pasting properties of starch.

How do starch chemical structures affect the gelatinization and retrogradation?

Studies have shown that different starches gelatinize at different temperatures which vary in a wide range. For example, potato starch, wheat starch, and waxy rice starch are known to have relatively low onset gelatinization temperatures, about 57–58°C, whereas high-amylose maize, ae waxy maize, and normal rice starches have high onset gelatinization temperature at about 71°C (Table 1). Onset gelatinization temperatures of normal maize and waxy maize starches are similar (~64°C), and that of normal glacier, waxy, and high-amylose glacier barley starches are also similar (59–60°C). These results confirm that increasing amylose contents do not cause an increase in gelatinization temperature. When the amylopectin structures of two starches are similar, increasing amylose contents is known to slightly decrease the gelatinization temperature. This can be attributed to amylose being interspersed among amylopectin molecules and interrupts the crystalline structure of starch granules.

Branch chain lengths of amylopectin and their distributions play the major role on affecting the gelatinization temperature of starch. Without other structural differences, such as phosphate monoester contents, a starch which contains longer branch chain lengths displays a higher gelatinization temperature. For example, high-amylose maize starches and ae-waxy maize starch, containing longer branch chains, display substantially higher gelatinization temperatures. In contrast, waxy and sweet rice starches have short branch chains and display low gelatinization temperatures.

Branch chain-length distributions of amylopectin (proportions of short and long branch chains) also significantly affect starch gelatinization temperature. Profiles of high-performance anion-exchange chromatography equipped with a post-column enzyme reactor and a pulsed amperometric detector (HPAEC-ENZ-PAD) [3, 4] have shown that most starches display a shoulder at DP 18–20 [5, 6]. On the basis of 3.5 Å for each glucose anhydrous unit, a branch chain of DP 19 has a chain length of about

66.5Å, equivalent to the full length of the crystalline region in amylopectin clusters obtained by neutron scattering studies (7). We have observed that a lower population ratio of branch chains with DP 18–20 compared with the population of peak chain-length (vary from DP 12 to DP 16) results in a lower gelatinization temperature of the starch. HPAEC-ENZ-PAD histograms of debranched amylopectins of high-amylose maize starch and ae-waxy maize starch display a shoulder of DP 18–20 at about the same intensity level as the peak chain length (DP 16), indicating a large proportion of branch chains extending full length of the crystalline region. Consequently, the amylopectin crystallites of the high-amylose maize and ae-waxy maize starch have fewer

Table 1

Thermal properties of starch gelatinization determined by differential scanning calorimetry[a]

Type	T_o[b] (°C)	T_p[c] (°C)	T_c[d] (°C)	ΔH[e] (J/g)
Normal maize	64.4 ± 0.4[sd]	69.4 ± 0.2	80.4 ± 0.4	13.2 ± 0.2
Waxy maize	64.2 ± 0.2	69.4 ± 0.1	81.2 ± 0.2	15.8 ± 0.2
Du waxy maize	65.6 ± 0.5	73.6 ± 0.1	88.3 ± 0.0	16.3 ± 0.3
Ae waxy maize	71.3 ± 0.2	78.8 ± 0.4	95.8 ± 0.7	18.8 ± 0.2
Amylomaize V	71.0 ± 0.4	81.3 ± 0.4	112.6 ± 1.2	19.5 ± 1.5
Amylomaize VII	70.6 ± 0.3	NA	129.4 ± 2.0	16.2 ± 0.8
Normal rice	71.1 ± 0.4	75.9 ± 0.5	87.6 ± 0.4	15.9 ± 0.6
Sweet rice	59.1 ± 0.4	64.7 ± 0.4	77.4 ± 0.6	15.8 ± 0.3
Waxy rice	57.1 ± 0.5	63.2 ± 0.5	80.1 ± 0.6	15.3 ± 0.1
Wheat	57.5 ± 0.4	61.7 ± 0.3	73.9 ± 0.4	11.3 ± 0.1
Barley	57.3 ± 0.2	60.3 ± 0.2	71.1 ± 0.3	10.2 ± 0.6
Waxy amaranth	70.4 ± 0.4	75.1 ± 0.0	83.3 ± 0.2	13.2 ± 0.5
Cattail millet	67.6 ± 0.6	72.0 ± 0.1	83.3 ± 0.2	15.4 ± 0.5
Mung bean	69.7 ± 0.1	72.3 ± 0.2	84.2 ± 0.3	12.5 ± 0.4
Chinese taro	67.9 ± 0.2	72.8 ± 0.6	88.0 ± 0.6	16.4 ± 0.2
Tapioca	62.4 ± 0.2	67.7 ± 0.5	86.2 ± 0.3	15.7 ± 0.5
Potato	58.2 ± 0.1	61.5 ± 0.1	73.8 ± 0.5	17.3 ± 0.1
Lotus root	61.1 ± 0.6	66.3 ± 0.8	77.9 ± 0.6	15.2 ± 0.5
Green leaf canna	59.3 ± 0.3	65.4 ± 0.4	80.3 ± 0.3	15.5 ± 0.4
Green banana	69.3 ± 0.3	72.6 ± 0.3	80.4 ± 0.3	18.4 ± 0.5
Water chestnut	59.3 ± 0.6	70.4 ± 0.8	87.4 ± 0.9	14.9 ± 0.2

[a] The values are averages of at least three starch samples with at least three replicates of each sample.
[b] Onset temperature.
[c] Peak temperature.
[d] Completion temperature.
[e] Enthalpy of starch gelatinization.
[sd] Standard deviation.

defects caused by the presence of short chains. The crystallites are, thus, more difficult to melt and gelatinize at a higher temperature. In contrast, wheat starch and barley starch display a distinguishable shoulder of DP 18–20 at a substantially lower population level than that of peak chain length of DP 11 and 12. The large proportion of short chains present in the crystallites, causing defects to the crystallites, results in substantially lower gelatinization temperatures (57–59°C).

Phosphate monoester derivatives are found in amylopectin of many starches, mostly tuber, root and legume starches. Phosphate monoesters are covalently attached mainly to carbon-6 of glucose which is at least nine glucose units away from the branch linkage (reducing end) [8, 9]. Results obtained from X-ray crystallography [10], DSC thermal properties [11], and Naegeli dextrin [12] have shown that the phosphate monoesters are located in the crystalline region. Starch phosphate monoesters each carries two negative charges; the phosphate groups repel one another and destabilize the starch crystalline structure, thus, reduce the gelatinization temperature. The best known example is potato starch. Potato amylopectin has one of the longest average branch chain length, but because the amylopectin carries a large number of phosphate monoesters (~0.08% phosphorus), it has a very low gelatinization temperature at 57°C.

Methods of starch isolation also affect the gelatinization temperature of starch. We have observed difference between waxy amaranth starch isolated by alkaline method [13] and by enzymatic method [14]. The same starch isolated by alkaline method displayed an onset gelatinization (T_0) of 70.6°C with an enthalpy change of 16.3 J/g, whereas the one by enzymatic method displayed T_0 of 66.7°C and an enthalpy change of 13.2 J/g. The difference can be attributed to alkaline treatment causing damage to the crystalline structure of the starch.

Retrogradation rate of starch is mainly dependent on branch chain length of amylopectin and phosphate monoester derivatives. Starches which have very short average branch chains tend to have slow retrogradation rates. Examples are waxy and sweet rice starches and waxy amaranth starch. Starches with long branch chains and high-amylose contents have high tendency to retrograde, such as high-amylose maize, high-amylose barley and ae-waxy maize starch. du-Waxy maize starch, which has a relatively short average chain length but possesses some very long branch chains, also displays a fast retrogradation rate.

How do starch chemical structures affect the pasting properties?

Amylose is known to be present radially in a starch granule and intertwined with amylopectin [15, 16]. Lipid contents in cereal starches are found to correlate positively with the amylose contents [17]. Up to 50% of amylose has been found complexed with

lipids in a single helical conformation [18]. Therefore, the amylose content of starch significantly affect starch swelling and pasting properties.

For all the cereal starches investigated by using an amylograph, the pasting temperature increase with the increase of amylose content. For example, onset pasting temperatures of waxy maize, normal maize, and high-amylose maize V starches are 69.5°C, 82°C, and 95°C, respectively (Figure 1). Onset pasting temperatures of waxy rice and normal rice starches are 64.1°C and 79.9°C, respectively (Figure 2). The increased onset pasting temperature can be attributed to amylose-amylopectin interaction. This interaction in cereal starch is further enhanced by amylose-lipid complex. As a consequence, the amylose restricts the swelling of starch granule after gelatinization. Viscosity development is delayed to a higher pasting temperature. Peak viscosities of cereal starches are also reduced with the increase of amylose content as demonstrated in maize (Figure 1) and in rice starches (Figure 2) containing different amylose contents.

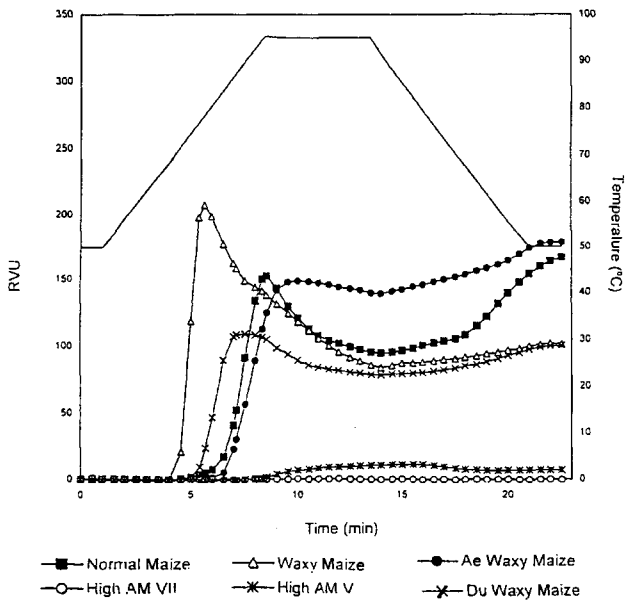

Fig. 1. Rapid Visco-Analyzer pasting profiles of various maize starches.

Increasing amylose contents, however, reduces shear thinning and results in a higher hot-past viscosity. This phenomenon is related to restricted granule swelling. When a starch granule is not fully swollen, it is less fragile and can resist shear force and retains integrity. Increasing amylose also increases set-back viscosity, a difference

in viscosity between hot-past viscosity and final viscosity after cooling. Set back is a phenomenon attributed to amylose in the solution forming a gel network matrix.

Branch chain lengths of amylopectin also affect pasting properties. Examples are shown in waxy maize, du waxy maize starch, and ae waxy maize (Figure 1). All three waxy starches contain no amylose, but branch chain lengths of the three differ. Waxy maize, du waxy maize, and ae waxy maize starch consist of average chain length of DP 23.5, DP 23.1, and DP 29.5, respectively. du Waxy maize starch consists of a small number of very long branch chains, up to DP 80, whereas waxy maize starch consists of no detectable chains longer than DP 73. ae Waxy maize starch has a large number of long chains to DP 84. With the increase of long branch chains, the pasting temperature of du waxy maize and ae waxy maize starch increase. The onset pasting temperatures of waxy maize, du waxy maize, and ae waxy maize are 69.5°C, 75.7°C, and 83.2°C, respectively. Peak viscosity of the three starches are 205 Rapid ViscoAnalyzer unit (rvu), 109 rvu, and 162 rvu, respectively, and the shear-thinning of the starches decrease to 121 rvu, 32 rvu, and 12 rvu, respectively. These results suggest that the presence of very long branch chains in starch also retain the integrity of swollen granules and resist to shear thinning.

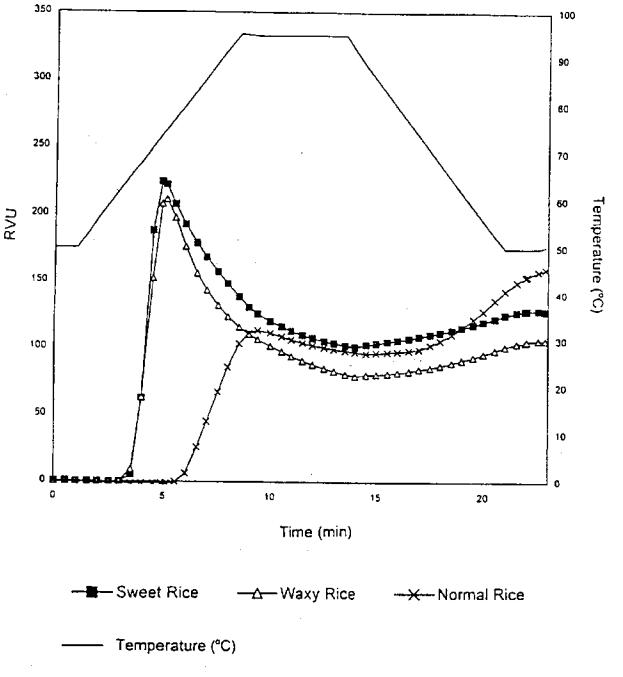

Fig. 2. Rapid Visco-Analyzer pasting profiles of waxy, sweet, and normal rice starches.

Starch phosphate monoesters enhance the peak viscosity and clarity of starch pastes, resulted from their charge repelling. The best example in nature is potato starch. Potato starch displays a very high peak viscosity of 702 rvu, compared with 152 rvu of normal maize starch and 173 rvu for tapioca starch. As a result of highly swelling of starch granules, potato starch paste also suffers a substantial amount of shear thinning of ~537 rvu. Phosphate monoester derivatives also enhance the stability of starch paste, slowing down starch retrogradation.

In contrary to the general observation that waxy starch has a higher peak viscosity than its normal starch counterpart, waxy potato starch has a lower peak viscosity and a slightly higher onset pasting temperature than does normal potato starch (Figure 3). Waxy potato starch has a slightly lower phosphate monoester content (0.066%) and slightly shorter branch chain lengths. The difference in their peak viscosity is mainly attributed to that amylose in the normal potato starch intertwine with amylopectin and hold the integrity of highly swollen granules, which results in the extremely high peak viscosity. Without amylose, waxy potato starch granules disperse promptly and, thus, does not reach to the same level of peak viscosity as does normal potato starch.

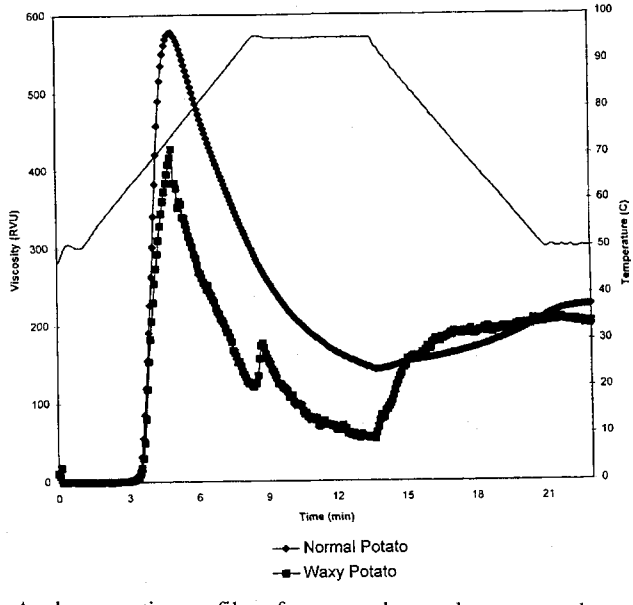

Fig. 3. Rapid Visco-Analyzer pasting profiles of waxy, and normal potato starches.

In contrast to phosphate monoesters, phospholipids have opposite effects on starch paste properties. Phospholipids are powerful complexing agents, which form helical complex with amylose and with long chains of amylopectin. As a result of the helical complex formation with amylose, starch granule swelling is retarded and di-

splays a very low peak viscosity, such as for wheat and barley starch. Wheat and barley starches have very low peak viscosity of 104 rvu and 88 rvu, respectively.

In conclusion, there is a better understanding of how starch structures control the gelatinization and pasting properties. Experimental results have shown that branch chain length and distribution govern the gelatinization temperature, enthalpy changes, rates of retrogradation, and pasting temperature and paste viscosity. Amylose contents predominantly affect pasting properties and rate of retrogradation. Phosphate monoester derivatives significantly affect the gelatinization, retrogradation, and pasting properties, and phospholipids increase the pasting temperature and reduce the peak viscosity.

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WPŁYW CHEMICZNEJ STRUKTURY SKROBI NA KLEIKOWANIE SKROBI

Streszczenie

Zanalizowano budowę chemiczna wielu odmian skrobi łącznie z zawartością amylozy, rozmiarami cząsteczek amylopektyny, długością łańcuchów w rozgałęzieniach oraz zawartością monofosforanu i fosfolipidów. Zbadano też kleikowanie i retrogradację tych skrobi. Wyniki badań pokazały, że tempperaturą kleikowania rządzi długość łańcuchów stanowiących rozgałęzienia amylopektyny i ich rozmieszczenie. Łańcuchy o przeciętnej długości i wysoki stosunek rozgałęziających łańcuchów krótkich (DP 11-16) do łańcuchów długich (DP 18-20) najprawdopodobniej odpowiadają za niską temperaturę kleikowa-

nia. Skrobie zestryfikowane kwasem fosforowym (monoestry) także mają niższą tempeaturę kleikowania. Przy tej samej strukturze amylopektyny wzrost zawartości amylozy obniża temperaturę kleikowania. Na tę temperaturę ma także wpływ metoda izolowania skrobi. Zawartość amylozy wpływa też na temperaturę tworzenia past. Zwykłe skrobie zbożowe zawierające lipidy i fosfolipidy mają wyższe temperatury tworzenia past, niższe maksymalne lepkości i mniej są rozrzedzane ścinaniem niż ich woskowe odpowiedniki. Zwykła skrobia ziemniaczana bez lipidów ma wyższą maksymalną lepkość niż ziemniaczana skrobia woskowa. Długość odgałęzień w amylopektynie także wpływa na tworzenie past przez skrobię. Bardzo długie łańcuchy ograniczają pęcznienie skrobi , podwyższają temperaturę tworzenia past i obniżają rozcieńczanie ścinaniem. Skrobie estryfikowane kwasem fosforowym mają niższe temperatury tworzenia past i podnoszą lepkość przez odpychanie ładunku. W przeciwieństwie do tego fosfolipidy przez skompleksowanie z amylozą i długie odgałęzienia w amylopektynie ograniczają pęcznienie skrobi i obniżają lepkość kleików i past.