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Physicochemical properties of hydroxypropyl derivative from corn and amaranth starch

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Abstract

Hydroxypropylation of starches is known to impart useful physicochemical properties that are advantageously utilized both in food as well as in non-food applications. The alteration in these properties is not only dependent on the molar substitution, but is species–specific as well. The present work compares the pasting properties of hydroxypropyl derivative prepared from corn starch and waxy *Amaranthus paniculatas* starch. The properties studied were swelling power, Brabender characteristics, paste clarity and freeze–thaw stability. A remarkable improvement in freeze–thaw stability of both the starches was the most significant finding of this work. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Hydroxypropyl derivatives; Physicochemical properties; Corn starch; Amaranth starch

1. Introduction

Modification of native starch by hydroxypropylation imparts some useful physicochemical properties, which increases its range of applications in different food as well as non-food applications. Hydroxypropylation renders a hydrophilic character when introduced into the starch granule and it is known to weaken or strain the internal bond structure that holds the granules together (Tuschoff, 1987). This reduction in bond strength is reflected in starch pasting temperature. Increasing degree of hydroxypropyl substitution lowers the pasting temperature, until the product swells in cold water. As the molar substitution (MS) increases from 0.4 to 1.0, granular hydroxypropyl starch exhibits better dispersibility in cold water (Rutenberg & Solarek, 1984). The unique property of modified starch is also evidenced in improved freeze–thaw or cold storage stability (Tuschoff, 1987). Here the hydrophilic nature of the hydroxypropyl group keeps the water in the starch paste from separating or synerisis when subjected to freeze/thaw cycling.

Hydroxypropylation results in the inhibition of ordered structures in the starch pastes, thus retarding retrogradation, and resulting in a more fluid paste with improved clarity. Because of the increased viscosity stability thus imparted, these starches are also referred to as stabilized starches. The resistance to high temperatures, low pHs and mechanical shear can be increased and viscosity stability can be improved by cross-linking of hydroxypropyl starch (HPS) (Zhou, Zhang & Fan,1991). However, this combination of modifications require careful control of the modification steps to make possible the 'tailoring' of starch products for very specific application conditions.

Incorporation of hydroxypropyl groups in the starch chains primarily in the amorphous region changes its granular and molecular structure. The penetration and absorption of water into the starch granules is facilitated, and increases the initial rate of plasticization of the amorphous regions of modified granules as compared with unmodified granules (Seow & Thevamalar,1993). This also increases the tendency of gelatinization. Thus, with a much less quantity of water under proper processing conditions (high temperature and pressure e.g. in extrusion or in alkaline conditions), HPS can form films that have low tensile strength but increased clarity. The elongation and burst strength are also increased, and the folding endurance is maintained (Rutenberg & Solarek, 1984). Film strength can be improved by using other plasticizers in combination with water (Soest & Knooren, 1997). Hydroxypropylation does not change the response of starch to microwave radiation, since the dielectric properties are unaltered by such treatment (Miller, Gordon & Davis, 1991).

In the present work, hydroxypropyl starch, prepared from corn and amaranth starch with five different MS varying from 0.025 to 0.13 were chosen for some studies on its paste properties.

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Table 1
Swelling power characteristic of HPSC and HPSA

Sample	Swelling power[a]	
	Corn starch	Amaranth starch
Native	1.0	1.15
HPS of MS:		
0.025	1.09	1.96
0.050	1.14	2.21
0.075	1.35	2.2
0.100	1.53	2.07
0.130	2.54	4.33

[a] Results were expressed relative to native corn starch which was assigned a swelling power of 1.0.

2. Materials and methods

HPS prepared from corn and amaranth starch as per our earlier communication (Pal, Singhal & Kulkarni, 2000), were analyzed for the paste properties.

2.1. Determination of swelling power

This was done as per the method of Wootton and Manatsathit (1983). 0.45 g of the sample was mixed with 5 ml distilled water in a 10 ml measuring cylinder. The volume of the sediment was then measured after 24 h at room temperature. Results were expressed relative to native corn starch which was assigned a swelling power of 1.0.

2.2. Brabender characteristics of HPS

Temperature and viscosity relationship was studied on 5% suspension (22.5 g in 450 ml) of starch samples (native and modified) on Brabender Viscoamylograph (model PT 100) using the following regimen: The samples sample was heated from 30 to 95°C at a heating rate of 1.5°C/min, at a bowl speed of 75 rpm, held at 95°C for 30 min and then cooled back to 30°C at 1.5°C/min. The results are interpreted with respect to gelatinization (or pasting) temperature, peak viscosity, viscosity at 95°C, viscosity after holding at 95°C for 30 min and cold paste viscosity at 30°C.

Table 2
Effect of hydroxypropylation on the paste clarity of corn and amaranth starch. Results are Mean ± SD of three individual determinations

Sample	Transmittance (% T at 650 nm)	
	Corn starch	Amaranth starch
Native	7.8 ± 0.05	8.80 ±.0.10
HPS of MS:		
0.025	16.3 ± 0.3	9.6 ± 0.33
0.050	24.5 ± 0.03	10.3 ± 0.40
0.075	21.8 ± 0.16	9.1 ± 0.32
0.100	26.2 ± 0.23	9.2 ± 0.15
0.130	27.9 ± 0.19	44.2 ± 0.06

2.3. Determination of paste clarity

This was done as per the method of Craig, Maningat, Seib and Hoseney (1989). HPS (50 mg) was passed through a standard sieve of 60 mesh and suspended in 5 ml water in a 10 ml cotton plugged test-tube. It was then placed in a boiling water bath for 30 min with thorough shaking every 5 min. After cooling to room temperature, the percent transmittance (% T) at 650 nm was determined in a Hitachi U-2001 spectrophotometer.

2.4. Freeze–thaw stability of HPS

Freeze–thaw stability of HPS samples was studied by allowing the gelatinized starch paste to alternate freezing and thawing (freezing for 24 h at −18°C and thawing for 1.5 h at 30 ± 2°C) (White, Abbas & Johnson,1989). 5% HPS pastes were prepared by heating a starch sample in required amount of water at 95°C water bath for 30 min and poured in a previously weighed 10 ml centrifuge tube. Weight of the centrifuge tubes was taken and subsequently frozen. Tubes were subjected to required freeze–thaw cycles, followed by centrifugation at 6000 rpm for 30 min. The percentage of water separated after each freeze–thaw cycle was measured. The weight of water was measured and the extent of syneresis was expressed as the percentage of water separated (Eliasson & Kim, 1992).

$$\text{Syneresis (\%)} = [\text{Water separated (g)/Total weight of sample (g)}] \times 100$$

Unmodified and HPS of low MS (<0.075) starch gel were studied for successive six freeze–thaw cycles. But, for highly substituted starch samples, tubes were centrifuged for selected number of freeze–thaw cycles to allow them for exhibition of first synersis.

3. Results and discussion

Swelling power and clarity of different HPS samples from both the starch sources compared to native starch are tabulated in Tables 1 and 2.

Incorporation of hydroxypropyl group into the starch chains are capable of disrupting inter-and intra-molecular hydrogen bonds, thereby weakening the granular structure of starch leading to an increased acceptibility of the starch granules to water. Besides this, the substituted starches are further more easily hydrated because the hydrophilic groups are incorporated. These two factors would lead to higher swelling power of HPS as compared to native starches. This is also in accordance with already available literature (Wootton & Manatsathit, 1983). HPSA had a much higher swelling power than HPSC at similar MS. This is due to the waxy nature of amaranth starch. Amylopectin is well known to contribute to greater hydration, as indicated by the restricted swelling of normal starches when compared to

Table 3
Brabender viscosity characteristics of HPS samples

Samples	Gelatinization temperature/ Pasting temperature (°C)	Peak viscosity (BU)	Viscosity at 95°C (BU)	Viscosity after holding at 95°C for 30 min (BU)	Viscosity after cooling to 30°C (BU)
Native corn	74.5	220	220	320	860
HPSC of MS					
0.05	56	430	150	110	320
0.075	53	405	150	120	400
0.10	52	70	65	65	70
Native amaranth	66.2	80	80	100	90
HPSA of MS					
0.050	55.5	80	80	80	85
0.075	55.5	50	50	60	70
0.100	53.5	50	50	60	68

their waxy counterparts (Leach, 1965), and the effect seems to have been pronounced on hydroxypropylation. This can be easily seen from the swelling power of 4.33 of HPSA as compared to 2.54 for HPSC at similar MS of 0.13.

Percent transmittance of 5% solutions of HPS is a measure of clarity. This was measured for both corn and amaranth starch, before and after hydroxypropylation. It was observed that, HPSC showed a significant increase in clarity as compared to native starch. However, no such trend was observed for amaranth starch. No significant effect of MS on the paste clarity was observed with both the starches. The only exception was HPSA of MS 0.130, where the clarity was significantly higher as compared to all the starches in the study. This is due to the fact that HPSA of MS 0.130 was almost gelatinized completely. The clarity of native amaranth was better when compared to native corn, and can be explained by greater swelling of amaranth starch, which allows more light to pass through the granules, instead of being reflected. This is because the starch molecules dissociate and the ability of the granules to reflect light diminishes. The same explanation holds true on the effect of introduction of the hydroxypropyl group in corn and amaranth starches. The changes to granular and molecular structures induced by hydroxypropylation facilitated penetration and absorption of the starch granules, which ultimately leads to more swelling of starch and resulting in more transmittance of light (Craig et al., 1989). For waxy amaranth starch solution, it is also possible that with the incorporation of hydrophilic hydroxypropyl group, the starch dissolution rate may have increased, and during dissolution starch molecules had a collapsed conformation which may also associate to form junction zones. The light was then reflected from these zones and made the solution less clear compared to hydroxypropyl corn starch (Craig et al., 1989).

Table 3 shows the Brabender characteristics of native corn and amaranth starches and that of the hydroxypropyl derivatives having MS of 0.05, 0.075 and 0.1. It was observed that there were significant differences between the native amaranth and corn starch viscograms, as well as with native and their modified starches. Amaranth starch always showed a lower gelatinization temperature than corn starch. Amylose content and starch granule size have been reported to be factors which influence starch gelatinization temperature. Probably high amylose content of corn starch was responsible for the strong associative forces in the granules, which prevented penetration of water inside the granules, thus delaying gelatinization temperature. Gelatinization temperature found for corn starch and waxy amaranth starch, was found to be more or less similar with the earlier reports (Zobel, 1984; Lorenz, 1981). It was also observed that the pasting temperature decreased gradually with an increase in MS for both the starches. This is also supported by the literature (Wootton & Manatsathit, 1984). This can be easily explained by the fact that the hydroxypropyl group being hydrophilic in nature facilitates penetration of water molecules inside the starch granule by weakening the granular structure, which eases the formation of gel (Seow & Thevamalar, 1993).

The gel formed from native corn starch dispersions was highly viscous as compared to that of native amaranth, as evidenced by the higher peak viscosity of corn starch gel. Thermal gelation of amylose were mainly responsible for the peak viscosity, which in turn depended on the swelling power and cohesive forces present in the starch granular structure. Peak viscosity of amaranth starch has been reported to be higher than corn starch (Bhattacharyya, Singhal & Kulkarni, 1995) from our laboratories. The contrary result obtained in the present work can only be explained to be due to the biological variation in samples that are frequently encountered. Peak viscosity of corn starch paste increased with an increase in MS up to 0.075 compared to native corn, after which at an MS of 0.10, there was a decrease in the same. The hydrophilic group caused loosening of the network allowing additional water to enter into the starch micelle (a cluster of starch granules). The micelle remained intact, holding the granules together in enormously swollen networks; thus the increase in hydration volume resulted in higher viscosity (Islam & Azemi, 1997). So in this case, cohesive forces in the starch granular

Table 4
Effect of hydroxypropylation on the freeze thaw stability of corn and amaranth starches

Sample	Percentage synersis[a]					
	1st cycle	2nd cycle	3rd cycle	4th cycle	5th cycle	6th cycle
Corn starch						
Native	30.57 ± 0.30	38.20 ± 0.10	41.14 ± 0.60	50.17 ± 0.45	57.30 ± 0.12	65.70 ± 0.35
HPSC of MS:						
0.025	Nil	14.72 ± 0.09	36.42 ± 0.15	40.21 ± 0.21	45.72 ± 0.24	52.42 ± 0.30
0.050	Nil	Nil	Nil	4.8 ± 0.05	19.2 ±0.11	28.9 ± 0.10
0.075	Nil	Nil	Nil	Nil	9.79 ± 0.14	11.16 ± 0.10
0.100	Nil	Nil	Nil	Nil	Nil	1.124 ± 0.07
Amaranth starch						
Native	Nil	Nil	12.45 ± 0.09	23.10 ± 0.17	31.31 ± 0.15	45.75 ± 0.25
HPSA of MS						
0.025	Nil	Nil	5.03 ± 0.05	10.21 ± 0.14	14.52 ± 0.12	Nil
0.050	Nil	Nil	Nil	Nil	Nil	1.58

[a] Results are mean ± SD of three determinations.

structure still remained intact after incorporation of hydroxypropyl group. But HPSC of MS 0.10 showed remarkable decrease in peak viscosity, probably caused by very weak cohesive forces in the granular structure due to incorporation of higher amount of hydroxypropyl group.

The breakdown of both of the native starch paste was not significant. For native corn and amaranth starch, viscosity still remained at 220 and 80 BU, at 95°C and even after holding for 30 min at 95°C. On the contrary, peak viscosity dropped down to 150 BU for HPSC samples of MS 0.05 and 0.075, when the starch paste reached 95°C. This was probably due to greater susceptibility of HPS towards prolonged stirring at elevated temperature compared to the native starches due to higher swelling power. HPSC of MS 0.1 did not show any breakdown on holding to 95°C and the viscosity remained more or less constant at 65 BU. This is probably due to its lower peak viscosity compared to other HPSC samples.

Again, the setback value or cold paste viscosity of starch gel after cooling reflects the retrogradation tendency of starch, which is influenced by the amylose content. Very low amylose content of amaranth starch used in this experiment, leads to weak intermolecular forces within the granules on cooling, giving almost nil setback value. This is also supported by the literature (Perez, Bahnassey & Breene, 1993). Cold-paste viscosity also showed a significant decrease as MS was increased due to retarded retrogradation. Poor retrogradation with HPSC of MS 0.1 resulted in a very minor increase in cold-paste viscosity. The fact of retarding retrogradation on hydroxypropylation was already reported for potato starch (Perera & Hoover, 1999).

Table 5
Number of cycles required to exhibit first synerisis by hydroxypropyl derivatives of corn and amaranth starch of higher MS

Sample	Cycle number	Observations
HPSC of MS 0.130	5	No separation
	7	No separation
	9	1.06% synersis
HPSA of MS:		
0.75	9	No separation
0.100	9	No separation
	16	No separation
	21	No separation
0.130	19	No separation
	2	No separation

In the case of amaranth starch, there was no significant change in viscograms of native and modified one. A very negligible amount of amylose content of amaranth starch rendered it to be less susceptible towards formation and breakdown of the starch paste, as well as the setback value. Thus, a more or less stable gel was formed with native amaranth and so hydroxypropylation could not bring out any significant effect on native starch paste.

Freeze–thaw stability of native and hydroxypropyl starches, subjected to alternate freeze–thaw cycles is illustrated in the following Table 4. Unmodified native corn and amaranth starch showed syneresis from the first and second cycle respectively. With increasing MS, the resistance to synersis improved, as indicated by the increased number of freeze–thaw cycles showing the delay in synersis. This was also supported by the literature (Kim, Muhrbeck & Eliasson, 1993). The poor freeze–thaw stability exhibited by unmodified starch indicates extensive retrogradation during frozen storage. However, substitution improved the water holding capacity of starch gels by decreasing the extent of retrogradation. The ability of hydroxypropyl groups in reducing retrogradation could be attributed to steric effects imposed by the bulky hydroxyl groups which prevented proper alignment of starch chains for maximum retrogradation.

For HPS of higher MS, further cycles were carried out for exhibition of first synersis and results obtained (Table 5) indicated no separation for HPSA of MS 0.100 and 0.13, even after 21st and 22nd cycles. For HPSC of MS 0.13, first indications of synerisis was observed only after the 9th cycle. Freeze–thaw cycle indicates the storage stability at low temperatures and one such cycle is equivalent to 2–3 weeks of frozen storage (Kite, Maywald & Schoch, 1963). These results suggest HPSA of MS 0.10 and 0.13 to be excellent thickeners for frozen foods.

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