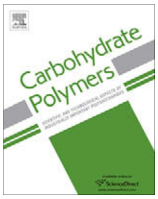
Carbohydrate Polymers 80 (2010) 725–732

Contents lists available at ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol



Effect of acetylation and dual modification on physico-chemical, rheological and morphological characteristics of sweet potato (*Ipomoea batatas*) starch

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ARTICLE INFO

Article history:
Received 6 October 2009
Received in revised form 30 November 2009
Accepted 11 December 2009
Available online 16 December 2009

Keywords:
Acetylation
Acetyl content
Dual modification
Morphology
Rheological characteristics

ABSTRACT

Chemical modification of sweet potato (*Ipomoea batatas*) was carried out by acetylation using vinyl acetate ranging from 4% to 10% and dual modification using propylene oxide at specific level of 7% followed by adipic acid anhydride at levels ranging from 0.05% to 0.12%. Degree of substitution ranges between 0.018–0.058% and 0.020–0.034% for acetylated and dual-modified starch samples, respectively. There was significant increase in water binding and oil-binding capacities, solubility, paste clarity, gel strength due to modification, however, rupture strength, gel elasticity and adhesiveness decrease in both modified starches. Analysis of SEM revealed that the modification altered starch morphology. Acetylation brought about slight aggregation or cluster formation of granules with deep groove in the central core region whereas in dual-modified starches there were present a number of aggregates of starch granules with development of few blister like appearances along with protuberances on their surfaces.

1. Introduction

Starches have many useful properties as a food ingredient but the native starches have limitations that reduce their use at the industrial level. The diversity of the modern food industry and the enormous variety food products require that starch would be able to tolerate a wide range of processing techniques as well as various distribution, storage and final preparation conditions. These facts motivated the employment of modified starches as important functional ingredients in processed foods in recent years because of their improved functional properties over unmodified starches (Smits, Ruhnau, Vliegenthart, Utrecht, & van Soest, 1998; Sodhi & Singh, 2005). Starch modification, involves the alteration of the physico-chemical characteristics of the native starch to improve its functional characteristics which can be used to tailor starch to specific food applications (Hermansson & Svegmark, 1996; Light, 1989).

Modification of starch, both by cross-linking and substitution modify the starch physico-chemical, rheological, morphological characteristics and improve the functional properties as per the requirement of the food products (Raina, Singh, Bawa, & Saxena, 2006; Swinkels, 1985; Wurzburg, 1986; Yeh & Yeh, 1993; Yiu, Loh, Rajan, Wong, & Bong, 2008). Lii, Tsai, and Tseng (1996) reported that the major influencing factor on the rheological and physiological characteristics is the amount of amylose leached out in the process. The amount of acetyling and cross-linking reagent necessary to give starch products with desirable properties will vary, depending on the starch base used, the cross-linking reagent, the reaction efficiency of the cross-linking reagent, the level of hydroxypropyl ether substitution on the starch base and a specified range of final modified starch properties (Wattanchant, Muhammad, Hashim, & Rahman, 2003). Microscopy (light and SEM) has played an important role in increasing understanding of granular structure of modified starches. It has been used to detect structural changes caused by chemical modifications and the most substituted regions in starch granules (Kaur, Singh, & Singh, 2004).

The demand of modified starch in India is around 27,500 tones per annum with a growth rate of 8–9% per annum (Anon, 2006). The main source of starch is corn, but the availability of corn to the Indian starch industry is decreasing day by day because of increased demand by industries involved in the production of breakfast cereals and snacks. For this reason it has becoming necessary to utilize non-conventional starches such as tubers starch to fill this gap. Sweet potato is an important crop in many developing countries, which is seasonal, cheaper, available in abundance, and can be used in the production of modification starch (Singh, Raina, Bawa, & Saxena, 2005). A few studies have been reported on native and modified sweet potato starch (Oladebeye, Oshodi, & Oladebeye, 2009; Takeda, Takunaga, Takeda, & Hizukuri, 1986). Sweet potatoes are rich in starch (6.9–30.7% w/b) and starch production is the main industrial utilization of sweet potatoes (Chen, Schols, & Voragen, 2004). Considering the above facts, the present investigation was carried out to study the effectiveness of chemical

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doi:10.1016/j.carbpol.2009.12.018

modification in preparation of acetylated and dual-modified sweet potato starches, which can be suitably used for various industrial food applications.

2. Materials and methods

2.1. Raw martial

Sweet potato is a seasonal crop and comes in the local market in the month of November and remains for a period up to 60 days. The raw material (reddish purple cylindrical variety) was procured from the local farm of Sangrur, Punjab and stored under refrigerated condition in the department laboratory.

The analyses of starch were carried out for moisture, crude protein ($\%N \times 6.25$), and ash content by the official methods, 15-A, 8-12, and 32-10 of (AACC, 2000). The total starch content was determined by the method of Chiang and Johnson (1977). Isolation of sweet potato starch was carried out by the method as described by Singh et al. (2005). The chemicals used for analysis were of Analytical Grade and were procured from M/s. Brightways Chemicals, Chandigarh (India).

2.2. Amylose content

The amylose content was determined by the method described by Scott, Hugh, and Colin (1998). A 0.1 g (w/b) sample (powdered form) was weighed. To this 1 ml of distilled ethanol was added. Then 10 ml of 1 N NaOH was added and left overnight. The volume was made up to 100 ml in the next day with distilled water. 2.5 ml of this extract was than taken and to this, about 20 ml distilled water was added followed by three drops of phenolphthalein and titrated against 0.1 N HCl. Than 1 ml iodine reagent was added, volume was made up to 50 ml and color was read at 590 nm. For standard graph, 0.2, 0.4, 0.6, 0.8, and 1 ml of amylose (1 mg/ml) was taken and the color was developed. One milliliter of iodine reagent was diluted to 50 ml with distilled water for a blank.

2.3. Calculation

Absorbance corresponds to 2.5 ml of the test solution = x g amylose

$$100\,\text{ml contains} = (x/2.5) \times 100\,\text{g amylose} = \text{amylose}\ (\%)$$

2.4. Modification of starch

Modification of sweet potato starch was carried out by substitution of starch with vinyl acetate and dual modification with propylene oxide (PO) and adipic acid anhydrate.

2.5. Acetylation

The acetylation (esterification) of sweet potato starch was carried out according to the method of Raina et al. (2006). Native starch (162 g, dry basis) was placed in a 500 ml beaker and 220 ml distilled water was added at 25 °C, to obtain a 42.4% w/w (db) starch suspension. The mixture was stirred with a magnet stirrer until homogeneous slurry was obtained. The pH was adjusted to 8.0 by adding drop wise 3% aqueous sodium hydroxide solution. Then the required amount of vinyl acetate (4%, 7.5% and 10%, on starch, db) was added drop wise, while simultaneously, 3% Sodium hydroxide was added to maintain the pH at 8.0–8.4 with continuous stirring. When the addition of the vinyl acetate was complete, the pH was adjusted to 4.5 with 0.5 N HCl to terminate the reaction. The slurry was filtered under vacuum through Buckner funnel. The filtered cake was washed with five volumes of distilled water. The resultant cake was dried at 45 °C for about 8 h to reach moisture content to less than 12%. The acetylated starch was ground and passed through 75 μm sieve, stored in airtight container for further use.

2.6. Dual modification

Dual modification of starch was carried out, by slight modification of method of Raina et al. (2006) by first reacting starch with propylene oxide (PO) followed by adipic acid anhydride. The etherification reaction was carried out at 40 °C for 24 h using (PO) in 40% w/w (db) starch slurry at pH 10.5 containing 15% sodium sulfate (db) (to restrict starch swelling during modification) and 5% sodium hydroxide (to maintain pH). The modified starch was cross-linked for 2 h using mixture of adipic acid anhydride.

Sodium sulfate (30 g, 15% dry starch basis, d/b) was added into water (300 ml) and stirred. When the salt was dissolved, sweet potato starch (200 g, dsb, equivalent to 40% starch solids in slurry) was added and the mixture was stirred to make uniform slurry. Then sodium hydroxide solution (5%) was added with vigorous stirring to maintain the slurry pH at 10.5. The propylene oxide (7%, on starch, db) was added and the slurry, which was at room temperature, was stirred for 30 min using magnetic shaker. The slurry was then transferred to glass bottles and contained in shaking incubator at temperature of 40 ± 2 °C with shaking rate of 200 rpm and held for 24 h. After that the pH (8.0–8.5) of the slurry was noted down and maintained and the cross-linking reagent (0.05%, 0.10% and 0.12% on starch, db) was added with vigorous shaking for 30 min. After that, the slurry was again transferred to glass bottles and the reaction was allowed to precede for 120 min at 40 ± 2 °C in incubator shaker with shaking rate of 200 rpm. The starch slurry was adjusted to pH 5.5 with 10% HCl to terminate the reaction. The starch was recovered under vacuum through Buckner funnel. The filtered cake was washed with five volumes of distilled water. The resultant cake was dried at 45 °C to reach moisture contents to less than 12% for about 8 h. The modified starch was ground and passed through 75 μm sieve, stored in airtight containers for further use.

2.7. Acetyl content

The acetyl group (AG, expressed as percentage on dry basis) and the degree of substitution (DS) of starch were determined as described by Smith (1967). A 5 g sample of starch was weighed, transferred to a 250 ml conical flask and dispersed in 50 ml-distilled water. Few drops of phenolphthalein indicator was added and titrated with sodium hydroxide 0.1 N to permanent pink color. Then 25.0 ml of 0.45 N NaOH was added to it and shaken vigorously for half an hour. The stopper and neck of flask was flushed with little distilled water and then the excess alkali was titrated with 0.2 N HCl to disappearance of pink color. 25.0 ml of 0.45 N NaOH was titrated as blank. Acetyl group and degree of substitution were calculated as follows:

$$\text{Acetyl group}\ (\%) = \frac{[(b - s) \times \mathrm{N} \times 0.043] \times 100}{W}$$

where b = volume of 0.2 N HCl used to titrate blank (ml), s = volume of 0.2 N HCl used to titrate sample (ml), N = normality of 0.2 N HCl, W = mass of sample (g, db)

$$\mathrm{DS} = 162 \times A/(4300 - 42A), \quad \text{where } A = \%\ \text{acetyl group (db)}$$

'DS' is defined as the average number of sites per glucose unit that possess a substituent group (Whistler & Daniel, 1995).

2.8. Water binding capacity (WBC)

WBC of the sweet potato starches was determined using the modified method of Medcalf and Gilles (1965). A suspension, 5 g (db) of starch in 75 ml-distilled water was agitated for 1 h and centrifuged at 3000 rpm for 10 min. The free water was removed from the wet starch, which was then drained for 10 min. The wet starch was then weighed.

$$\text{Water binding capacity }(\%) = \frac{\text{Weight of residual starch}}{\text{Weight of sample}} \times 100$$

2.9. Oil-binding capacity (OBC)

OBC of the sweet potato starches was determined using the modified method of Medcalf and Gilles (1965). A suspension, 5 g (db) of starch in 75 ml oil was agitated for 1 h and centrifuged 3000 rpm for 10 min. The free oil was removed from the wet starch, which was then drained for 10 min. The residue was then weighed.

$$\text{Oil-binding capacity }(\%) = \frac{\text{Weight of residual starch}}{\text{Weight of sample}} \times 100$$

2.10. Sediment volume

Sediment volume was determined by the method of Tessler. M. M. (1978). One gram of starch (db) was weighed into beaker and 95 ml of distilled water was then added. The pH of the starch slurry was adjusted to pH 7.0 using 5% NaOH or 5% HCl. The slurry was cooked in a boiling water bath for 15 min. Distilled water was then added to bring the total weight to 100 g. The mixture was then stirred thoroughly and transferred to a 100 ml-graduated cylinder. The cylinder was sealed with aluminium foil and the starch slurry was kept at room temperature for 24 h. The volume of the sediment, consisting of starch granules was then measured.

2.11. Swelling power and solubility Index

Swelling power was determined by the method of Schoch (1964). Starch was accurately weighed (2 g, db) into a pre-weighed 250 ml centrifugal bottle. Distilled water was added to give a total volume of water equivalent to 180 g. The starch was completely suspended by stirring at 200 rpm using a magnetic stirrer. After taking out the stirrer, the bottle was immediately placed in a temperature controlled water bath at 85 °C with continuously shaking at 200 rpm for 30 min. The centrifugal bottle was then dried and placed on a balance followed by the addition of distilled water to bring to a total weight of 200 g. After capping, the bottle was centrifuged for 15 min at 1000g. To measure solubility Index, 50 ml of the supernatant was transferred into an evaporating Petri-dish and dried overnight in a hot air oven at 105 °C. The dried residue was then cooled in desiccators and weighed for soluble starch. To measure the swelling power, the residual supernatant was carefully removed and discarded. The bottle with sediment paste was then weighed to give the weight of swollen starch granules. The result was expressed by the as:

$$\text{Swelling power }(\%) = \frac{\text{Weight of sediment paste} \times 100}{\text{Weight of sample on dry basis} \times (100 - \%\text{solubility})}$$

2.12. Paste clarity

The clarity (%T) of starch paste was measured using procedure of Lim and Seib (1993). A 1% aqueous suspension of starch near neutral pH was heated in boiling water bath for 30 min with intermittent shaking. After the suspension was cooled for 1 h at 25 °C, the light transmittance at 650 nm was read against water blank.

2.13. Color determination

The color of sweet potato starch (native and modified) was measured by Hunter color measuring system (Hunter Color Diff. Meter, Miniscan XE plus, Hunter Associates Laboratory Inc., USA). The starch was passed through a 100-mesh sieve before color estimation. A cylindrical plastic dish (58 mm in diameter and 15 mm in depth) containing the same quantity of dried samples was placed at the light port (50 mm in diameter). The information given by L^*, a^*, b^* and ΔE is generally expressed as the total color of powdered samples, with L^* representing the brightness or dullness, a^* for redness to greenness while b^* for yellowness to blueness.

$$\Delta E = \sqrt{\Delta L^2 + \Delta a^2 + \Delta b^2}$$

2.14. Rheological properties

The texture of gel (8% starch solids) was determined using Texture Analyzer (TAXT –2i) (Stable Micro Systems, UK). The following conditions were used for measurement of gel characteristics:

Mode: measure force in compression; option: return to start; pre-test speed: 3.0 mm/s

Test speed: 2.0 mm/s; post-test speed: 10.0 mm/s; distance: 15 mm; trigger type: auto – 15 g; data acquisition rate: 400 pps

To prepare gels, the procedure described by Takahashi, Maningat, and Seib (1989) was followed. All starches were adjusted to pH 6.5 using 5% NaOH or using 5% HCl solution before cooking from 30 to 95 °C, held at 95 °C for 30 min, and then cooled to 50 °C. The paste was then poured to a height of 2.7 cm into a cylindrical plastic container (diameter: 4.0 cm, height = 5.5 cm) and stored for 24 h at 4 °C and 25 °C. For gel strength measurement, when a trigger force of 15 g was attained the probe (cylindrical plunger; diameter: 5 mm) then proceeded to penetrate into the gel at a speed of 2.0 mm/s to a depth of 15 mm. During this penetration the force is shown to drop at the point where the gel breaks. Thereafter, the resulting forces are due to continuing penetration up to the required depth. The peak (positive) force (i.e., the rupture point of the gel) is taken and recorded as 'gel rupture strength' (or rupture force, N). A gel strength (N) measurement is taken at the initial stage of penetration, i.e., a point (in this case 3 mm) in the penetration where little gel deformation has occurred. The distance that the gel penetrated before its break occurred gave an indication of the gel's elasticity (mm), i.e., a short distance of penetration before break indicated a brittle gel whereas a large distance of penetration before rupture indicated a more elastic gel. When the probe was withdrawn from the sample, the total force, (gs, area under the negative region of the curve) required to do this was measured and recorded as the adhesiveness.

2.15. Morphology of starch

Morphology of the native and modified starch granules was evaluated by the scanning electron microscope (Hitachi S-3400 N, Japan) by the procedures suggested by Lares, Perez, and Gonzalez (1997). Starch samples were completely dried overnight (50 °C) and then suspended in ethanol to obtain 1% suspension. One drop of the starch–ethanol suspension was applied on an aluminium stub and stub was placed in dryer for 2 h. After drying, stubs were coated with gold–palladium (60:40). Then it was placed in microscope with an accelerating potential of 15 kV used during micrograph.

2.16. Statistical analysis

Excel software package (MS-Office XP) was used for data analysis. Analysis of variance (ANOVA) with Tukey's standardized range test was performed to examine the effect of modification on various physico-chemical and rheological properties of starches. Samples in triplicate were used and a significance level of $p \leqslant 0.05$ was applied.

3. Results and discussions

3.1. Analysis of native and modified starch

Analysis of native and modified starch is shown in Table 1. The moisture and ash contents of native and modified sweet potato starch sample varied from 8.70–11.90% (w/b) to 0.23–0.77% (w/b), respectively. The total starch content was 86.88% (wb) for native starch and for modified starch samples it varied from 87.23% to 87.90%. Protein present in native sweet potato starch sample was 0.3%, which decreases upon modification. Lawal (2004) explained that modification causes structural disintegration, which weakens starch granules, and this probably enhances protein, fiber and fat leaching from the granule. Amylose content of sweet potato starches has increased from 24.45% in native starch to 26.68% in acetylated starch but gets decreased in dual-modified starch. Singh, Kaur, and Singh (2004) reported that the presence of acetyl groups cause increase in amylose content estimation.

3.2. Physico-chemical characteristics

3.2.1. Acetyl content and degree of substitution (DS)

The acetyl content of sweet potato starches increases gradually during acetylation as compared to dual modification (Table 2), because the acetylation of starch during latter treatments were only due to the bi-functional nature of adipic acid anhydride (Raina et al., 2006). The acetyl content of acetylated sweet potato starch ranges from 0.47% to 1.548% and in dual-modified sweet potato starch (M_4–M_6) it varies from 0.524% to 0.89%. Chen et al. (2004), reported that acetylation of potato and sweet potato starch occurs in all the amorphous regions and also at the outer lamellae of crystalline regions rather than throughout the crystalline regions of the whole starch granule. The 'DS' of modified sweet potato starch varies from 0.018% to 0.058%.

3.2.2. Water binding capacity

It was observed that acetylation and dual modification has profound effect on water binding capacity of starch (Table 3). Water binding capacity of native starch was 77.38%, where as water binding capacity for acetylated starch (M_1–M_3) varies from 78.8% to 90.5%. The results are in agreement as explained by Singh et al. (2004). The water binding capacity is observed higher in the starch where amylose and amylopectin are loosely associated. The differences in degrees of availability of water binding sites among the starches may have also contributed to variation in water binding capacity (Wotton & Bamunuarachchi, 1978). The water binding capacity of dual-modified starches (M_4–M_6) varies from 67.5% to 82%. The water binding capacity was lower for starch sample M_4 which increase with increase in dual modifying agent. This may be due to effect of acetylation for the dual modification at the higher level of modification. Hoover and Sosulski (1986) explained that the engagement of hydroxyl groups, to form hydrogen and covalent bonds between starch chains, lowers water binding capacity as is case with native starch samples.

Table 2
Acetyl content and degree of substitution (DS) of modified starches.[a]

Starch samples	Acetyl content (%)	Degree of substitution (DS)
Native	NA	NA
M_1	0.470	0.018
M_2	0.720	0.027
M_3	1.548	0.058
M_4	0.524	0.020
M_5	0.710	0.027
M_6	0.890	0.034

[a] Samples in triplicate were taken.

3.2.3. Oil-binding capacity

Oil-binding capacity of native starch was 66.77% (Table 3), where as it varies from 77.67% to 82.69% and 74.35% to 78.90% for acetylated and dual-modified starches, respectively. It is observed that oil-binding capacity of modified starch was higher as compared to native starch sample but gets decrease at higher substitution level. In acetylated starch samples the oil-binding capacities gradually decrease because of reduction of the amorphous region in the starch granules. This reduces the number of available binding sites for oil in the starch granule. The results are in agreement with the findings of (Tian, Rickard, & Blanshard, 1993).

3.2.4. Sediment value

Sediment value of the native sweet potato starch sample was 32 as shown in Table 3. The sediment value of modified starch was lower than native starch sample. For M_1–M_3 samples sediment value varies from 20 to 27 where as for dual-modified starch samples M_4–M_6 value varies from 22 to 30. Similar results were observed by Raina et al. (2006) for acetylated and cross-linked rice starches who reported that the introduction of acetyl group decreases interaction between the starch molecules thus resulting in less sedimentation where as cross-linking inhibits swelling and thereby reduces the sediment volume.

Table 1
Analyses of sweet potato starch.[a]

Starch samples	Moisture (%)	Ash (%)	Total starch (%)	Protein (%)	Amylose (%)
Native	9.54b	0.30a	86.88a	0.300c	24.45b
M_1	10.80b	0.77d	87.67c	0.125a	26.68c
M_2	10.20b	0.40c	87.30b	0.137b	25.47c
M_3	9.80b	0.46b	87.90d	0.165b	25.34c
M_4	8.70a	0.49b	87.23b	0.168b	22.00a
M_5	9.08a	0.47b	87.42b	0.156b	20.98a
M_6	11.9c	0.42b	87.45b	0.125a	20.30a

Values denoted by different small letter in the same column differ significantly ($p \leqslant 0.05$).

[a] Samples in triplicate were taken.

Table 3

Physico-chemical characteristics of native and modified sweet potato starch.[a]

Starch sample	Water binding capacity (%)	Oil-binding capacity (%)	Sediment volume (ml)	Solubility (%)	Swelling power (%)	Paste clarity (%*T*)
Native	77.38b	66.77a	32d	4.70a	13.39ab	6.0a
M_1	78.8d	82.69c	27c	4.86a	15.46b	7.0bc
M_2	85.30c	80.45bc	23b	6.48b	16.37bc	7.2bc
M_3	90.30d	77.63b	20a	7.30c	18.62d	7.8d
M_4	67.50a	74.35b	30d	5.10a	9.99a	6.3a
M_5	77.00b	76.40b	24b	5.15a	12.21a	6.8b
M_6	82.00bc	78.90b	22ab	7.50c	13.28ab	7.5c

Values denoted by different small letter in the same column differ significantly ($p \leqslant 0.05$).

[a] Samples in triplicate were taken.

3.2.5. Swelling power and solubility index

The swelling power and solubility of native starch sample was 13.39% and 4.70%, respectively. The swelling power of acetylated starch (M_1–M_3) varies from 15.46% to 18.62% and solubility varies from 4.86% to 7.30%. It is observed from the Table 3, that swelling power of acetyl starch was higher than that of native starch. This is in agreement with Lawal (2004) and Raina et al. (2006) that acetylation increases swelling power. On the other hand swelling power of dual-modified sweet potato starch samples M_4–M_6 varied from 9.99% to 13.28% and solubility varies from 5.10% to 7.50% and was lower or not significantly different from native starch. It may due to the hydroxypropylation that will weaken the bonding between starch molecules, thus allowing more cross-linking reagents to react with the starch molecules (Morrison, Tester, Snape, Law, & Gidley, 1993; Wattanchant et al., 2003).

3.2.6. Paste clarity

It is observed from Table 3 that paste clarity of native starch sample 6.0% is significantly lower than modified starch. Paste clarity of acetylated starch samples (M_1–M_3) varies from 7.0% to 7.8%. In acetylated normal and high amylose starches chain association is inhibited which favors retention of amorphous character and high clarity (Betancur, Chel, & Canizares, 1997; Kaur et al., 2004). In the case of dual-modified sweet potato starch sample (M_4–M_6) the paste clarity varies from 6.3% to 7.5%, but the increase was lower than acetylated starch samples. Increase in %*T* after dual modification is due to chemical substitution of the hydroxyl groups in starch molecules due to bi-functional nature of adipic acid. Marked reduction of % transmittance of native starch is a result of retrogradation tendency (Singh, Kaur, & McCarthy, 2007).

3.2.7. Color

There was significant difference ($p \leqslant 0.05$) in color between different modified samples when compared to native starch sample. The *L*, *a* and *b*, values for native sweet potato starch sample were 93.878, 0.306 and 3.320, respectively (Table 4). For acetylated sweet potato starch (M_1–M_3), *L*, *a* and *b* values varies from 94.281 to 96.636, 0.168 to 0.225 and 3.062 to 3.268, respectively, where as *L*, *a* and *b* values for dual-modified sweet potato starch samples (M_4–M_6) it varies from 94.546 to 96.269, 0.124 to 0.228 and 3.009 to 3.184, respectively. From the data it is observed that *L*, *b* and values of acetylated starches were higher than dual-modified sweet potato starch samples. High *L* value (lightness) and chroma are desired in starches (Raina et al., 2006).

Table 4

Effect of treatments on color values of native and modified sweet potato starch.[a]

Treatments	*L*	*a*	*b*	ΔE
Native	93.878a	0.306e	3.320d	2.345c
M_1	94.281b	0.225d	3.268c	2.272bc
M_2	95.734c	0.190c	3.191ab	2.201b
M_3	96.636d	0.168b	3.062a	2.004a
M_4	94.546b	0.228d	3.184ab	2.799d
M_5	95.979c	0.164b	3.154b	2.646b
M_6	96.269d	0.124a	3.009a	2.118b

Values denoted by different small letter in the same column differ significantly ($p \leqslant 0.05$).

[a] Samples in triplicate were taken.

3.3. Rheological characteristics

The rheological characteristics of starch gel such as gel strength, rupture strength, gel elasticity and adhesiveness are shown in Table 5.

3.3.1. Gel strength

The modification has shown remarkable effect on the gel strength (mean force at 3 mm) at both 4 and 25 °C storage temperature. The gel strength of native starch sample was 0.183 N at 4 °C and 0.166 N at 25 °C. The values were lower than modified sweet potato starch at both storage temperatures. The gel strength of acetylated sweet potato starch stored at 4 °C had shown higher gel strength (0.216–0.256 N) than for those stored at 25 °C (0.146–0.235 N). The results are in agreement for acetylated and contrary for dual-modified starches (Kaur et al., 2004; Liu, Ramsden, & Corke, 1999). The dual-modified starch samples (M_4–M_6) stored at 25 °C had shown higher gel strength (0.240–0.251 N) than the acetylated starch samples (0.185–0.235 N), where as the substituted sample stored at 4 °C had shown higher gel strength as compared to dual-modified starch samples stored at same temperature. Raina et al. (2006) explained that substitution allows the starch to remain hydrated and increases the stability during low temperature storage.

3.3.2. Rupture strength

Rupture strength of starch gels of modified starch increases with increase in acetyl content but was lower than native starch at both storage temperatures. Increase in rupture strength was relatively higher for modified gels stored at 25 °C than for those stored at 4 °C, may be due to harder texture and decrease in elasticity for gels stored at lower temperature. The gel firmness is mainly caused by retrogradation of starch gels, which is associated with the synersis of water and crystallization of amylopectin, leading to higher rupture strength (Miles, Morris, Oxford, & Ring, 1985). Rupture strength of dual-modified starch samples was lower than the acetylated starch samples. This may be due to decrease in gel elasticity in the dual-modified starches as compared to acetylated starches (Raina et al., 2006).

3.3.3. Gel elasticity

The gel elasticity of native starch sample, 511.65 gs at 4 °C and 741.10 gs at 25 °C was higher than modified starch. The elasticity decreases gradually upon acetylation (M_1–M_3), i.e., 436.00–376.50 gs at 4 °C and 685.12–462.80 gs at 25 °C and in dual modi-

Table 5
Rheological characteristics of sweet potato starch gel.[a]

Sample	Temperature (°C)	Gel strength (N)	Rupture strength (N)	Gel elasticity (gs)	Adhesiveness (gs)
Native	4	0.183a	0.622d	511.65e	63.50d
M_1		0.216b	0.564a	436.00d	49.05c
M_2		0.239bc	0.570b	405.40c	43.05b
M_3		0.256cd	0.615d	376.50b	27.35a
M_4		0.207b	0.551a	352.60b	54.89c
M_5		0.226b	0.587c	309.70a	49.18c
M_6		0.239cd	0.596bc	301.20a	31.75a
Native	25	0.176a	0.785c	741.10d	80.52d
M_1		0.145a	0.596a	685.12c	58.78b
M_2		0.175a	0.617a	572.60b	41.49a
M_3		0.235b	0.642b	462.80a	34.80a
M_4		0.240b	0.557a	678.80c	73.40c
M_5		0.248b	0.600a	546.64b	67.34c
M_6		0.251b	0.611a	444.06a	52.77b

Values denoted by different small letter in the same column differ significantly ($p \leqslant 0.05$).

[a] Samples in triplicate were taken.

fication (M_4–M_6), 352.60–301.20 gs at 4 °C and 678.80–444.06 gs at 25 °C. The elasticity is lower for the gels stored at 4 °C than that of gels stored at 25 °C. This is due to increase in brittleness of gels stored at low temperature. Sodhi and Singh (2005) described that starches with higher degrees of substitution showed higher percent decrease in hardness of their gels. It was observed that the gel elasticity of acetylated starches was higher than dual-modified starches. Similar results were reported by Raina et al. (2006), for modified rice starch who explained that cross-linking strengthens the granules to resist rupturing and impart, short slave like structure.

3.3.4. Adhesiveness

The adhesiveness of native sweet potato starch 63.50 and 80.52 gs stored at 4 and 25 °C, respectively, was higher than modified starch samples stored at similar temperatures. Due to acetylation adhesiveness decreases from 49.05 to 27.35 gs and 58.78 to 34.80 gs for storage temperature 4 and 25 °C, respectively. Liu et al. (1999) and Raina et al. (2006) observed similar effects of acetylation in starches. Also there was gradual decrease in adhesiveness of dual-modified starch sample (M_4–M_6) i.e., 54.89–31.75 gs and 73.40–52.77 gs stored at 4 and 25 °C, respectively.

3.4. Morphological characteristics

The scanning electron micrograph (SEM) of native and modified starch is shown in Figs. 1a–g, (a–g). It is observed that the diameter of native sweet potato starch sample varies from 6 to 22 µm. The native sweet potato starch consisted of a mixed population of large, medium and small granules and exhibit in various shapes (oval, pentagonal, hexagonal) with smooth surface. The granules size of acetylated sweet potato starch sample M_1 varies from 4.8 to 16 µm, for M_2 it varies from 7 to 18 µm and for M_3 it varies from 5 to 23 µm. The acetylation brought about slight aggregation or cluster formation of granules. It is observed that few of acetylated granules developed a depression that resulted in slight fragmentation, indentation, and the formation of a deep groove in the central

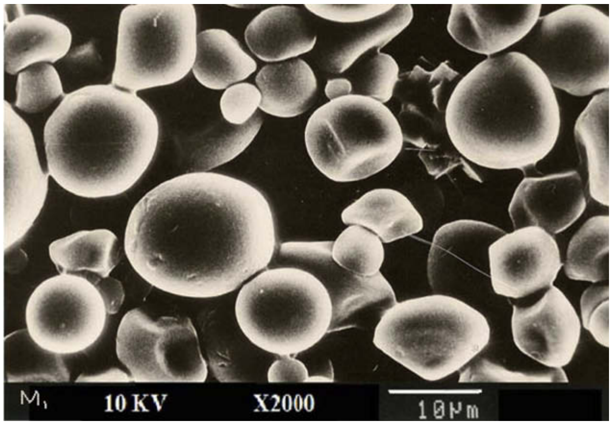

Fig. 1b. SEM of modified starch sample (M_1 – 4% vinyl acetate).

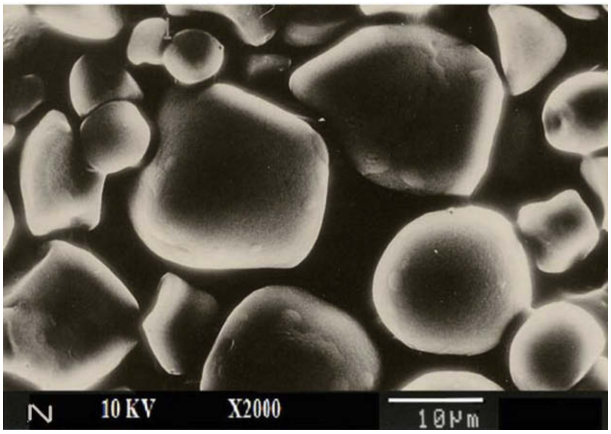

Fig. 1a. Scanning electron micrograph (SEM) of native sweet potato starch.

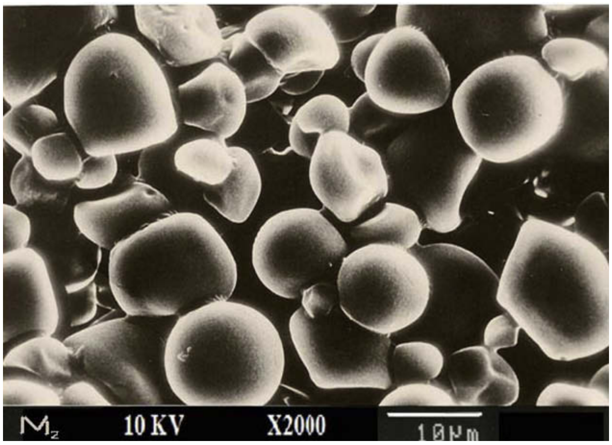

Fig. 1c. SEM of modified starch sample (M_2 – 7.5% vinyl acetate).

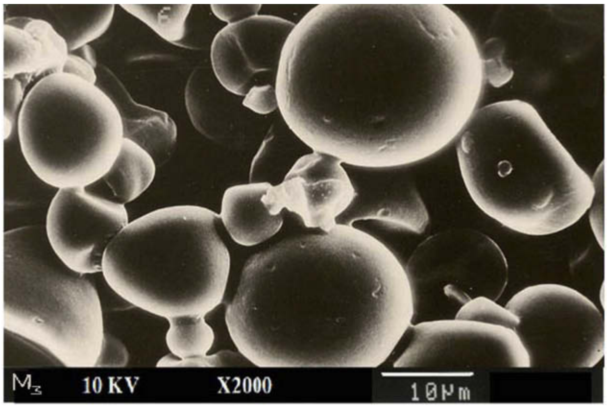

Fig. 1d. SEM of modified starch sample (M_3 – 10% vinyl acetate).

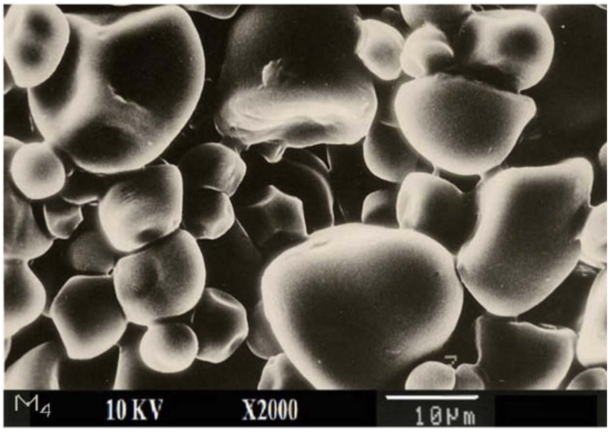

Fig. 1e. SEM of modified starch sample (M_4 – 0.05% Adipic acid and 7% Propylene oxide).

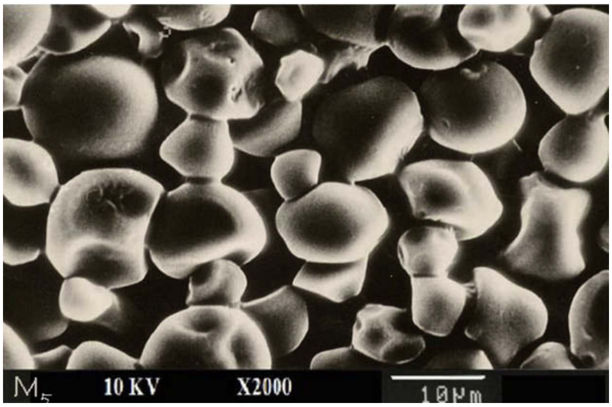

Fig. 1f. SEM of modified starch sample (M_5 – 0.10% adipic acid and 7% propylene oxide).

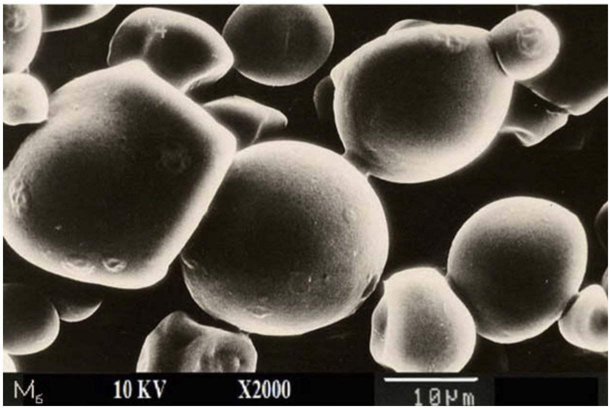

Fig. 1g. SEM of modified starch sample (M_6 – 0.12% adipic acid and 7% propylene oxide.

core region with granule fusion more pronounced in small size granules as reported by Kaur et al. (2004) and Singh, Chawla, and Singh (2007) in other starches.

For dual modified sample, granules diameter varies from 6 to 22 µm for M_4, 6 to 15 µm for M_5 and 7 to 22 µm for M_6. There were present a number of aggregates of starch granules, having granule fusion higher than acetylated starch. Granules developed few blister like appearances, small protuberances on their surfaces, and a deep groove in the central core region; appears as folded structures with their outer sides drawn inwards, giving the appearance of a doughnut Some what similar observations were reported by Singh, Kaur (2007) in potato starch.

4. Conclusion

The sweet potato could be an advantageous starting material for starch because of its continuous and low-priced supply. The acetyl contents and the degree of substitution obtained for modified starches were very low and permissible for application for edible purposes as prescribed by FDA. The result obtained from experiment shown that the chemical modification affects the composition and physico-chemical characteristics of sweet potato starch. Due to modification, total starch value gradually increased where as amount of protein decreases as compared to native starch. After modification of sweet potato starch, there was a significant increase in past clarity, swelling power and water binding capacity. Due to modification gel and rupture strengths increase at various temperatures where as gel elasticity and adhesiveness of get decreased. Acetylation produced films with good strength but the films with maximum strength in terms of puncture and tearing strength was formed with dual-modified starch. It was observed that morphology of sweet potato starch granule gets altered due to chemical modification. Further in food application all these modified starches can be used for development of different products depending on the quality requirement of the product, which could be evaluated with specific applications in them.

Acknowledgements

The first author greatly acknowledges the kind help and cooperation of Central Instrumentation Laboratory, Panjab University, Chandigarh.

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