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Functional, physicochemical and retrogradation properties of sword bean (*Canavalia gladiata*) acetylated and oxidized starches

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Abstract

The functional and physicochemical properties of native and chemically modified starches of Sword bean (*Canavalia gladiata*) were investigated. The starch yield was 31% (on whole seed basis). The chemical composition of the native starch is as follows: 0.17% crude protein, 0.08% crude fibre, 0.14% fat, 0.87% ash, carbohydrate determined by difference was 85.60%, while the energy value was 1437.64 KJ Kg^{-1}. The native starch was chemically modified by oxidation (with sodium hypochlorite) and acetylation (with acetic anhydride). The scanning electron micrograph SEM of the starches shows a smooth ellipsoids with slight indentation in the center of the granules, however, oxidation and acetylation causes rupture (<10%) of the granules. The water binding capacity of the modified starch increased after chemical modification in the following order:

Acetylated starch > Oxidized starch > Native starch

The solubility of all the starches increased as the temperature was increased with the Oxidized starch having the highest value. Swelling power measured from 50 to 90°C at 10°C intervals, also increased as the temperature increased among the starches. The order is similar to that recorded for the water binding capacity. The oil and water absorption capacity ranges from 2.9–3.6 g/g and 2.2–2.7 g/g, respectively, for all the starches. The pasting properties show the starches to be a Type C starch with restricted swelling which is typical of legume starches. Viscosity of the starch was increased by acetylation while oxidation reduces it. The gelatinization temperature (onset, peak and conclusion) was higher in the native starch than the chemically modified starches, while its enthalpy was lower.

Keywords: Sword bean; *Canavalia gladiata*; Acetylation; Oxidation; Starch; Functional properties

1. Introduction

Sword Bean (*Canavalia gladiata*) belongs to the e Pea family—*Fabaceae*. It originated either from southern Asia or Africa (Purseglove, 1968). It is relatively fast growing, usually producing a crop in 3–4 months. Sword bean is tolerant of a wide range of rainfall conditions: 700–4200 mm or ∼27–165 in., environmental conditions, and is well adapted to growth and survival in low-quality soils. Unlike most pulses, it is tolerant of leached nutrient-depleted lowland tropical soils, and resistant to most diseases and pests (Smart, 1976). Sword bean also tolerates acid soil conditions (pH 4.3–6.8) relatively well, and is more tolerant than most pulses of waterlogged soils or high salinity soil conditions (Smart, 1976; Spoladore & Teixeria, 1987).

In Africa, most especially in the interior South-Western Nigeria, it is usually used as green manure and cover crop, due to its adaptations to marginal soil conditions, including its nitrogen-fixing capabilities (Smart, 1976), which make it a species with promise for reclamation of impoverished tropical soils. The dried beans of Sword Bean are good sources of protein (22–29%) and starch (35–45%), with a good balance of amino acids (Spoladore & Teixeria, 1987).

Despite its desirable attributes, there has been little agronomic development of Sword bean, since its seeds are not extensively utilized as a food, due to its toxicity (Purseglove, 1968). This include the presence of growth-inhibiting protein substances, canavalin and concanavalin A (Con A) and the amino acid, canavanine in the seeds and foliage (Eknayake, Jansz, & Nair, 1999). Con A binds to mucosal cells lining the human digestive tract reducing the ability of the intestine to absorbs nutrients (Purseglove, 1968;

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Spoladore & Teixeria, 1987). It is for this reason that human consumption is best limited to only the younger foliage and pods of these beans.

There is therefore the need to explore alternative application of its seeds, most especially the starch, in the food and non-food industries. This quest becomes more urgent because corn remains the major source of starch for the chemical industries. About 64% of the world starch production was isolated from corn, 6% from potato, and about 6% from wheat, while the rest was obtained from sources such as cassava, yucca, sweet potato (Betancur, Gurrero, Camelo, & Ortiz, 2001). Application of this desirable but underutilized Sword bean starch in the industries will go along way to reduce the over-dependence on corn and other sources of starch in the industry. Native starch has many disadvantages which limit their wide application and their industrial use however; modified starches show better paste clarity and stability, increased resistance to retrogradation, and freeze-thaw stability (BeMiller, 1997).

The objective of this study, therefore, is to determine physicochemical and functional properties of the native Sword bean starch, and the effect of chemical modifications (acetylation and oxidation) on the starch properties.

2. Material and methods

2.1. Starch isolation

Sword bean was cultivated on an experimental plot at International Institute for Tropical Agriculture (IITA), Ibadan, Nigeria. The seeds were manually dehulled, and screened to remove stones and impurities. The seed were then dry milled and the flour stored in a refrigerator at 4 °C until further use. The starch was isolated from the bean flour by the procedure outline in Fig. 1.

2.2. Chemical modification of Sword Bean starch

The method of Sathe and Salunkhe (1981) was employed for the preparation of acetylated starch as follow: 100 g of prime starch were dispersed in 500 ml of distilled water and magnetically stirred for 30 min to obtain a uniform suspension. The pH was adjusted to 8.0 using 1 M NaOH. 10.2 g of acetic anhydride was then added slowly while maintaining constant stirring and monitoring the pH between 8.0–8.4. The reaction was allowed to proceed for additional 5 min after completion

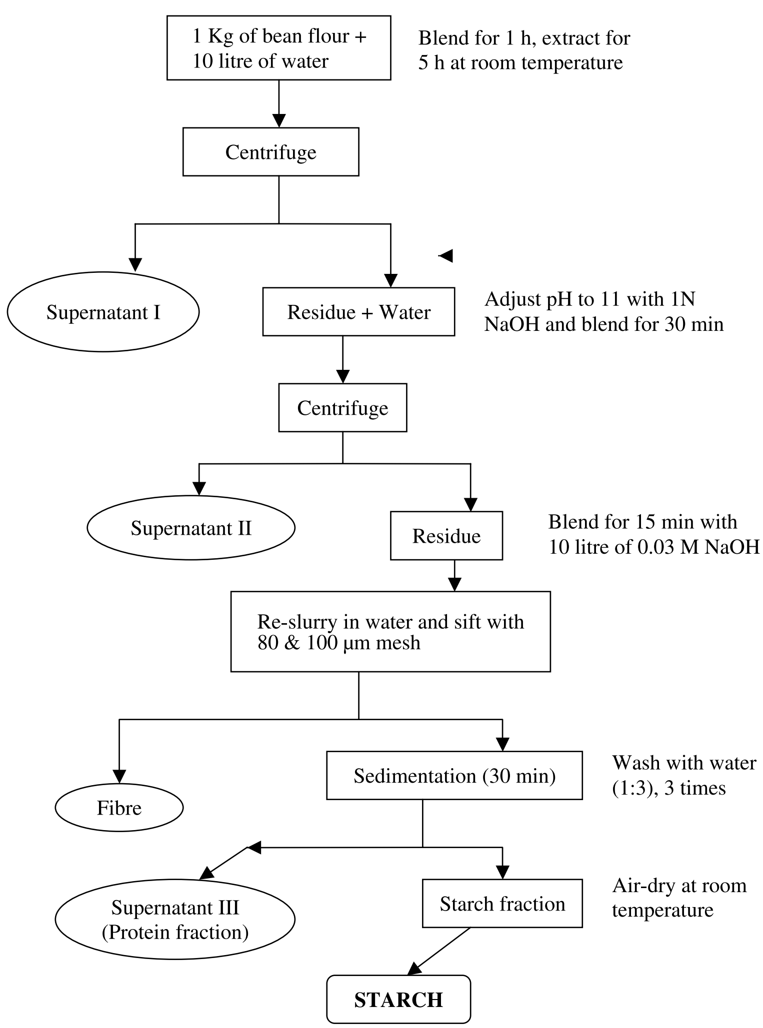

Fig. 1. Schematic diagram of the isolation of Sword bean starch.

of acetic anhydride addition. The pH of the slurry was finally adjusted to 4.5 with 0.5 M HCl and filtered through a Whatman filter paper #4. The residue obtained was washed five times with distilled water and air dried at room temperature. The determination of the degree of substitution of the acetylated starch was carried out by the procedure of Smith (1967).

Preparation of Oxidized starch (Sathe & Salunkhe, 1981) was carried out as follows: 100 g of prime starch was dispersed in 500 ml distilled water. The pH of the slurry was adjusted to between 9.0–9.5 using 3% NaOH. 10 g of NaOCl was added slowly over a period of 90 min while maintaining the magnetic stirring and constantly monitoring the pH between 9.0–9.5. Cooling was provided (crushed ice with NaCl) simultaneously. The reaction was allowed to proceed for 4 h after NaOCl addition was completed. The pH was then adjusted to 7.0 with 0.5 M HCl and the slurry filtered through Whatman filter paper #4. The residue was washed five times with distilled water and dried at room temperature. The degree of substitution of oxidized starch (carboxyl and carbonyl content) was determined using the procedure of Parovuori, Hamunen, Forsell, Autio and Powanen (1995).

2.3. Chemical analysis

AOAC (AOAC, 1990) method was employed for the determination of ash, moisture content, fibre content of the Sword bean seed and native starch. The nitrogen content was determined using the microkjeldahl method, and protein content was calculated as nitrogen $\times 6.25$. The fat content was obtained from a 4 h extraction with *n*-hexane. The moisture content was determined as the weight loss after oven drying at 60 °C for 4 h. The ash content was calculated from the residual weight after incinerating the sample in a muffle furnace at 550 °C for 5 h. Carbohydrate was determined by difference. The energy value was estimated in kilojoules by multiplying the protein, fat and carbohydrate percentages by the factors 16.7, 37.7, and 16.7, respectively (Eknayake et al., 1999). The pH of 30% (w/v) slurry of sample was determined using an Omega HPPX digital pH-meter.

2.4. Granule morphology

Granule morphology of the starch was studied by scanning electron microscopy (SEM). Samples were sputter-coated with Au/Pd using a vacuum evaporator (Ewards, Milano, Italy) and examined using a scanning electron microscope (Model 500, Philips, Eindhoven, The Netherlands) at 10 KV accelerating voltage using the secondary electron technique.

2.5. X-ray diffraction

X-ray diffractograms of starch powders were obtained with a Rigaku D-Max- 2200 X-ray diffractometer (Rigaku Denki Co. Tokyo, Japan). The scanning region of the diffraction angle was from 3 to 40°, with target voltage 40 kV, target current, 100 mA, and aging time 5 min.

2.6. properties

The method of Hallgreen (1985) was employed for the determination of the water retention capacity. Solubility and Swelling power was determined as described by Waliszewski, Aparicio, Bello and Monroy (2003). Oil and water absorption capacity of the starch was determined by the method of Beuchat (Beuchat, 1977). A Rapid Visco-Analyser model 3D (RVA; Newport Scientific Pty. Ltd., Warriewood, Australia) was used to determine the pasting properties of the starch in 25 g of distilled water underwent a controlled heating-and-cooling cycle under constant shear where it was held at 50 °C for 1 min, heated from 50 to 95 °C at 6 °C/min, held at 50 °C for 5 min.

The gelatinization parameters of the native and modified Sword bean starch were determined as follows: Water (11 μl) was added with a micro-syringe to starch (3.0 mg) in the DSC pans, which were then sealed, reweighed and allowed to stand for 2 h at room temperature before DSC analysis to attain an even distribution of water. The scanning temperature range and heating rates were 30–140 °C and 10 °C/min, respectively. In all measurements, the thermogram was recorded with an empty aluminum pan as the reference. The transition temperatures reported are the onset (T_o), peak (T_p), and conclusion (T_c). The enthalpy of gelatinization (ΔH) was estimated by integrating the area between the thermogram and a base line under the peak and was expressed in terms of Joules per gram of dry starch (Beuchat, 1977). The retrogradation properties of the starch was studied as follow: Water (3 μl) was added with a microsyringe to starch (3.0 mg) in the DSC pans, which were then sealed, reweighed and allowed to stand for 6 h at room temperature for moisture equilibration. The sealed pans were then heated (20–120 °C at 10 °C/min) to gelatinize the starch. The gelatinized samples were stored at 40 °C for 24 h to enhance the propagation of crystallites. Subsequently, the samples were equilibrated at room temperature for 2 h, and then rescanned in the calorimeter from 20–120 °C at 10 °C/min to measure retrogradation transition temperature and enthalpy (Ratnayake, Hoover, Shahidi, Perera, & Jane, 2001).

The method of Coffmann and Garcia (1977), as modified by Sathe and Salunkhe (1981) was employed for the determination of the gelation properties of the starches. Appropriate sample suspensions of 2, 4, 8, 10, 12, 14, 16, 18, and 20% (w/v) were prepared in 5 ml distilled water. The test tubes containing these suspensions were then heated for 1 h in a boiling water bath followed by rapid cooling under running cold tap water. The test tubes were then further cooled for 2 h at 4 °C. The least gelation concentration was determined as that concentration when the sample from the inverted tube did not fall down or slip.

3. Results and discussion

The chemical composition of Sword bean whole seeds and its native starch is presented in Table 1. Starch yield of the dehulled seed is 31%. This is similar to that obtained for Beach pea (Chavan, Shahidi, Hoover, & Perera, 1999), but

Table 1
Chemical composition of Sword bean seed and native starch (on dry basis)

Analysis	Composition	
	Whole seed	Native starch
Moisture content (%)	10.4	13.1
Crude protein (%)	22.7	0.2
Crude fibre (%)	7.3	0.1
Crude fat (%)	3.2	0.1
Ash content (%)	4.2	0.9
Carbohydrate (%)	52.2	85.6
Energy value (KJ Kg^{-1})	1372	1437
PH	7.9	6.6

Results are means of triplicate determination.

lower than the starch content of most legumes such as 35.56% obtained for baby lima bean (Vose, 1980), 44% for field peas, and 48% for Horsebeans (Bressani, Gomez, Garzia, & Eliaz, 1987). The crude protein value of the whole seed (22.70%) falls within range obtained for most legumes, and is comparable to that obtained by Eknayake et al. (1999) and Bressani et al. (1987) for the same species. The protein content of the native starch of Sword bean (0.17%) is lower than that of corn starch (>0.35%), which makes it feasible as raw material for production of glucose or fructose syrups, as it avoid interference with Maillard reactions (Chavan et al., 1999). The 0.14% fat content of

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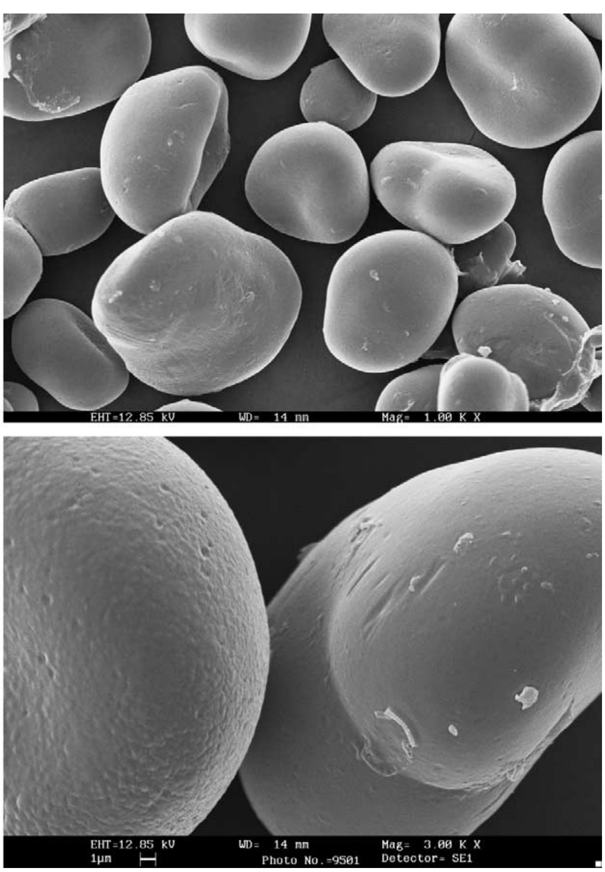

Fig. 2. (A) Scanning electron micrographs of Sword bean native starch at 1000× magnifications. (B) Scanning electron micrographs of Sword bean native starch at 3000× magnifications.

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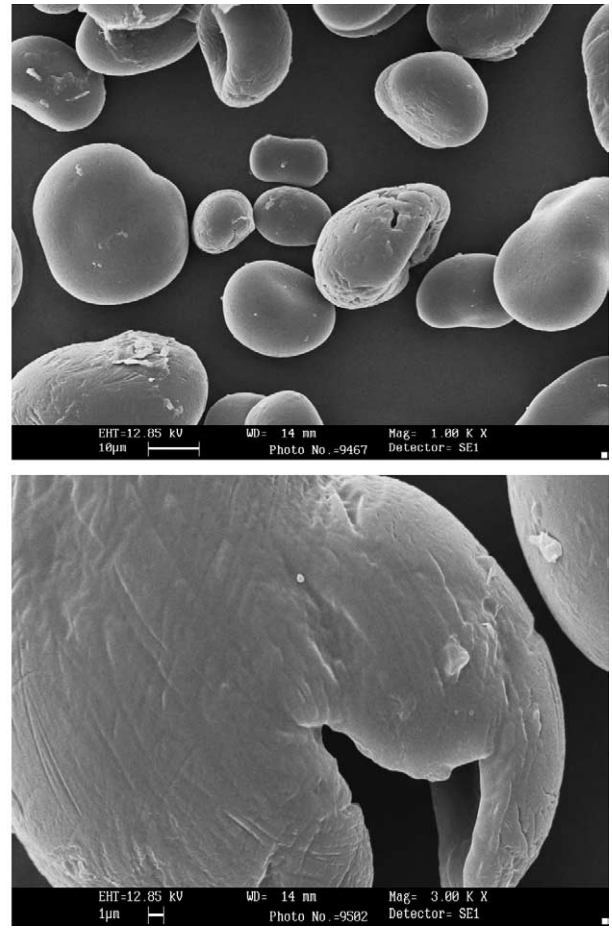

Fig. 3. (A) Scanning electron micrograph of Sword bean acetylated starch (SAC) at 1000×magnification. (B) Scanning electron micrograph of Sword bean acetylated starch (SAC) at 300×magnification.

the native starch is at par with that reported by Lorenz (1990), for quinoa (0.11%), barley (0.50%), and 1.10% for amaranth starch. Fat content has direct relationship with amylose-lipid complex formed during processing, and can lead to production of resistance starch (Sanchez-Hernandez, Slorza-Feria, Mendez-Montealvo, Paredes-Lopez, & Bello-Perez, 2002). The high ash content value of 4.22% in the whole seed (Table 1) may be an indication of presence of high quantity of minerals in the Sword bean seeds.

The scanning electron micrographs of the Sword bean starches (native and modified) at 1000 and 3000 × magnifications are presented in Figs. 2–4. For comparisons in size and morphology, all samples were photographed at magnifications of 1000 and 3000 times. Sword bean native starch (Fig. 2A, B) has smooth ellipsoids and indentation in their center. The surface of individual granules photographed at 3000 × magnification appears smooth (Fig. 2B). However, acetylation causes rupture (<10%) of the granules (Fig. 3A) giving the surface a rough appearance (Fig. 3B). Oxidation of the starch also causes rupture of the starch granules (Fig. 4A), producing cavity (<10%) in the centre of some of the granules (Fig. 4B). Since structure of starch granules are described as semi-crystalline with amorphous and crystalline regions, the phenomenon observed is probably due to the fact that oxidation

A

B

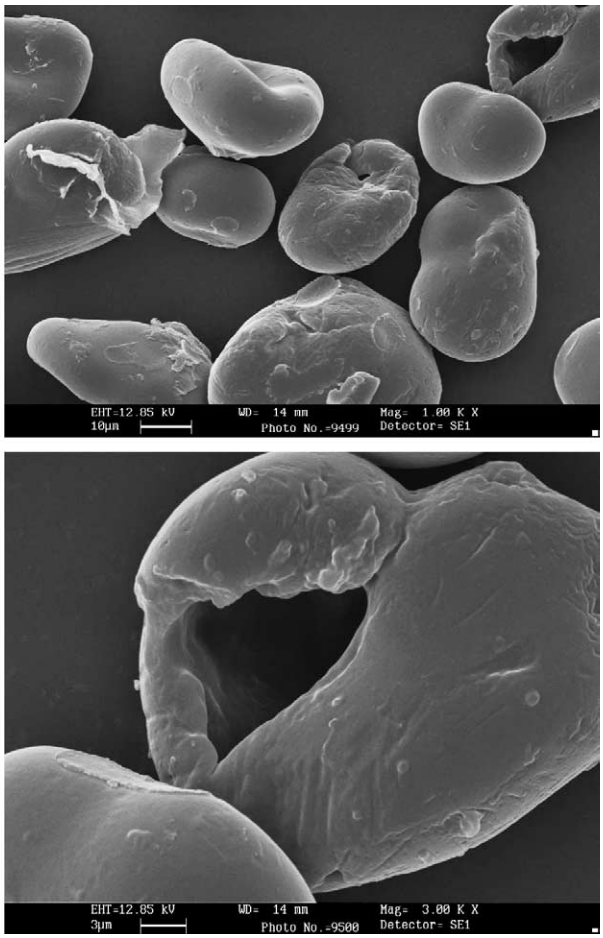

Fig. 4. (A) Scanning electron micrographs of Sword bean oxidized starch at 1000× magnification. (B) Scanning electron micrographs of Sword bean acetylated starch at 3000× magnification.

and acetylation attack the amorphous region preferentially, there by removing the region from the surface of the starch, which consequently leads to rupture of the granules.

The X-ray diffraction pattern of the native (SBN), acetylated (SAC) and oxidized (SOX) starch of the Sword bean is presented in Fig. 5. The native starch (SBN) exhibited the Type 'B' pattern with strong peak at 17.1 and weak peak at 26.4 Å. The oxidized starch (SOX) exhibited the Type 'C' X-ray pattern with strong peaks at 17.3 and 23.51 Å, and weak peak at 11.5 and 20.5. The acetylated starch also exhibited the Type 'C' X-ray, with strong peaks at 15.3, 17.3, and 23.45 Å, with weak peaks at 20.4 and 26.8 Å. Gidley (Gidley, 1987) suggested that the Type 'C' pattern is not a true crystalline polymorph but rather a mixture of 'A' and 'B' polymorphs. A fourth pattern, the 'V' pattern, arises from complexes formed by amylose with a variety of polar organic molecules (Zobel, 1988; Zobel, Young, & Rocca, 1988).

The degree of substitution of acetylation and oxidation of the Sword bean starch are 0.14 and 0.08, respectively. The results of water binding capacity of the native and chemically modified starches heated from 50–90 °C are shown in Table 2. There was increase in the water binding capacity of the entire starch as the temperature was increased, however, the chemically modified starches recorded higher water binding capacity than the native starch, at all temperature studied. Oxidation and acetylation of Sword bean enhanced the water binding capacity of Sword bean starch because hydrophilic groups were incorporated into the native starch. Acetylated starch recorded the highest increase at all temperature values studied.

The solubility power of the Sword bean starch at different temperature (Fig. 6) shows that there was an increase in the solubility of the starches as the temperature increased, with the oxidized starches having highest solubility at all the temperature studied. This is probably due to the weakening of the starch granules during hypochlorite oxidation leading to improved solubility (Shieldneck & Smith, 1976), although, the solubility characteristic of the acetylated starch is dependent upon the degree of substitution and polymerization (Krucer & Rutenberg, 1976).

The swelling power of native and chemically modified Sword bean starch measured from 50 to 90 °C at 10 °C intervals (Fig. 7) shows an increased swelling power of all starches as the temperature increased, in the following order: Acetylated starch > Native starch > Oxidized starch. Leach, McCowen and Schoch (1950) proposes that bonding forces within the granules of a starch affects its swelling power. This is probably why the oxidized starches of Sword bean has lower swelling power to its native starch, as these highly associated starch granules with an extensive and strongly bonded micellar structure display relatively great resistance towards swelling.

The oil absorption capacity of the native, oxidized, and acetylated Sword bean starches are 2.90, 3.60, and 3.20 g/g, while its water absorption capacities are 2.20, 2.50, and 2.70 g/g, respectively (Table 3). The ability of starch to absorb water is an indication of its stability moisture most especially in

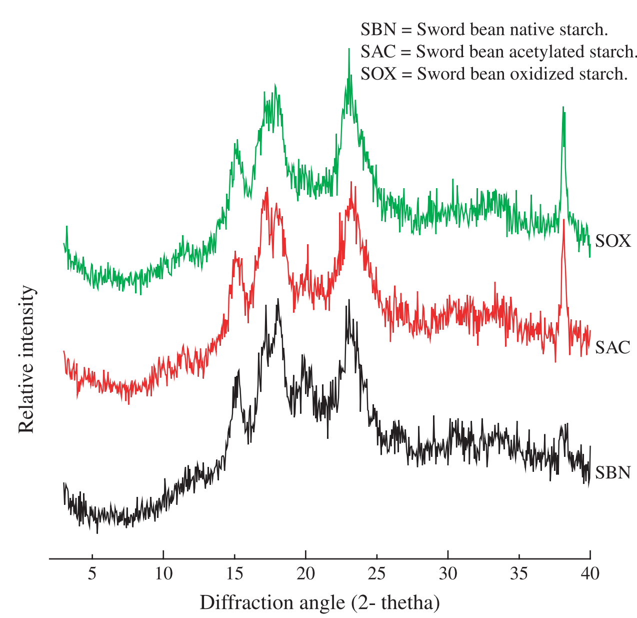

Fig. 5. X-ray diffraction pattern of Sword bean oxidized and acetylated starch.

Table 2
Water binding capacity of native and chemically modified Sword bean starch heated from 50 to 90 °C (g of water retention g^{-1} of starch × 100) on dry basis

Type of starch/temp	50 °C	60 °C	70 °C	80 °C	90 °C
Native	10.8	18.6	28.6	41.2	45.9
Oxidized[a]	18.4	27.6	35.9	48.2	50.4
Acetylated[b]	24.0	32.1	48.7	57.4	59.9

Results are means of triplicate determinations.
[a] Degree of substitution = 0.08.
[b] Degree of substitution = 0.14.

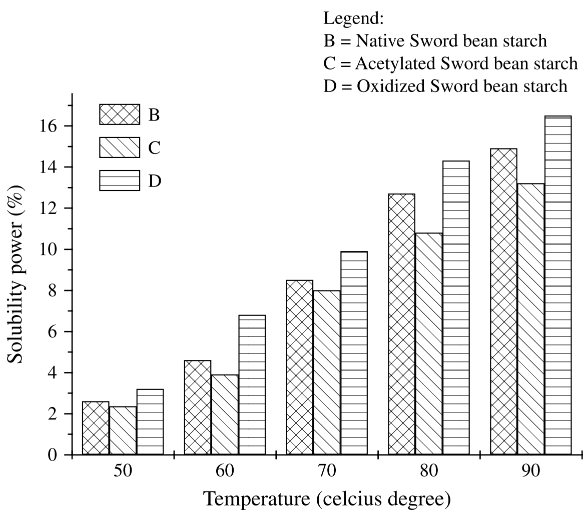

Fig. 6. Solubility power of Sword bean native and chemically modified starch (on dry basis).

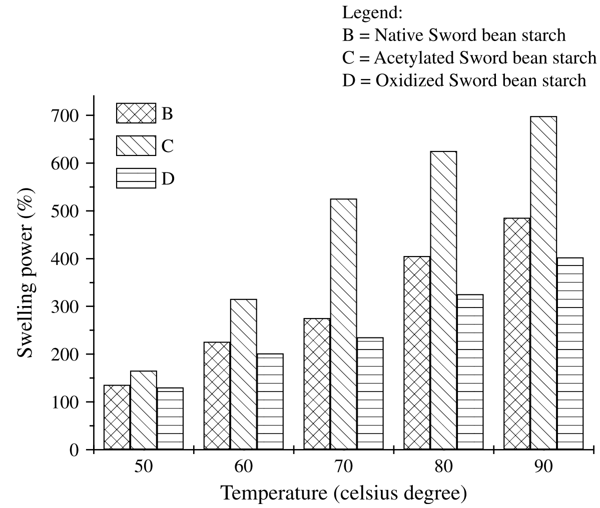

Fig. 7. Swelling power of Sword bean native and chemically modified starch (on dry basis).

the food industry, while oil absorption capacity of starch reveals its emulsifying potentials.

The pasting properties and curves of the native and modified Sword bean starch are presented in Table 4 and Fig. 8A–C. Based on Schoch and Maywald (1968) classification of viscosity of starches, Sword bean native and modified starches can be classified as Type C starches with restricted swelling (typical of legumes), and has high peak viscosity (438.33 RVU), breakdown (180.90 RVU), and setback (169.33 RVU). Acetylation increases the viscosity while oxidation reduces it. The RVA viscosity of the oxidized starch is much lower than that of the native and acetylated starch of Sword bean. The lower breakdown (difference between peak and trough viscosity) imply higher hot paste stability (resistance to shear thinning during cooking) for the oxidized starch. Wilhelm, Themeier and Lindhauer (1998) postulates that alkaline media damaged starch structure irreversibly and reduce paste viscosity.

The gelatinization temperature of the native and chemically modified starches of Sword bean is presented in Table 5. From the result, the onset, peak and conclusion temperature was higher in the native starch, than that of the chemically modified starches (Native starch > Oxidized starch > Acetylated starch), but with lower ΔH. Gelatinization involves the uncoiling and melting of the external chains of amylopectin that are packed together as double helices in clusters (Chavan, Shahidi, Hoover, & Perera, 1999), while ΔH is due mainly to the disruption of the double helices rather than the long range disruption of crystallinity (Cooke & Gidley, 1992). The gelatinization temperature and enthalpy of the starch depends on the microstructure and degree of crystallinity within the granule size and the amylose to amylopectin ratio (Chavan et al., 1999). The reduction in the gelatinization temperature values of the chemically modified starch of Sword bean is probably due to the granule size and mechanical damage to granules (as revealed by the SEM) during chemical modification (Chavan et al., 1999).

Table 6 shows the retrogradation characteristics of Sword bean native, acetylated, and oxidized starch. The temperature

Table 3
Oil and water absorption capacity of Sword bean native and chemically modified starch (on dry basis)

Starch type	Water absorbed (g/g)	Oil absorbed (g/g)
Native starch	2.2±0.2[a]	2.9±0.3[c]
Oxidized Starch	2.7±0.3[b]	3.2±0.4[d]
Acetylated starch	2.5±0.3[a]	3.6±0.5[e]

Results are means of triplicate determination; Means which is followed by same superscript along the same column indicates there is no significant difference at $P < 0.05$.

Table 4
Pasting properties of Sword bean native and chemically modified starch (on dry basis)

Analysis/type of starch	Native starch	Oxidized starch	Acetylated starch
Peak viscosity, PV (RVU)	438.0	399.0	766.0
Trough viscosity, TV (RVU)	257.0	264.0	366.0
Breakdown (PV-TV), (RVU)	181.0	135.0	401.0
Final viscosity, FV (RVU)	427.0	479.0	521.0
Setback (FV-TV), (RVU)	169.0	215.0	156.0
Peak time (min)	4.0	4.0	4.0
Pasting temperature (°C)	64.0	64.0	65.0

Results are means of triplicate determination.

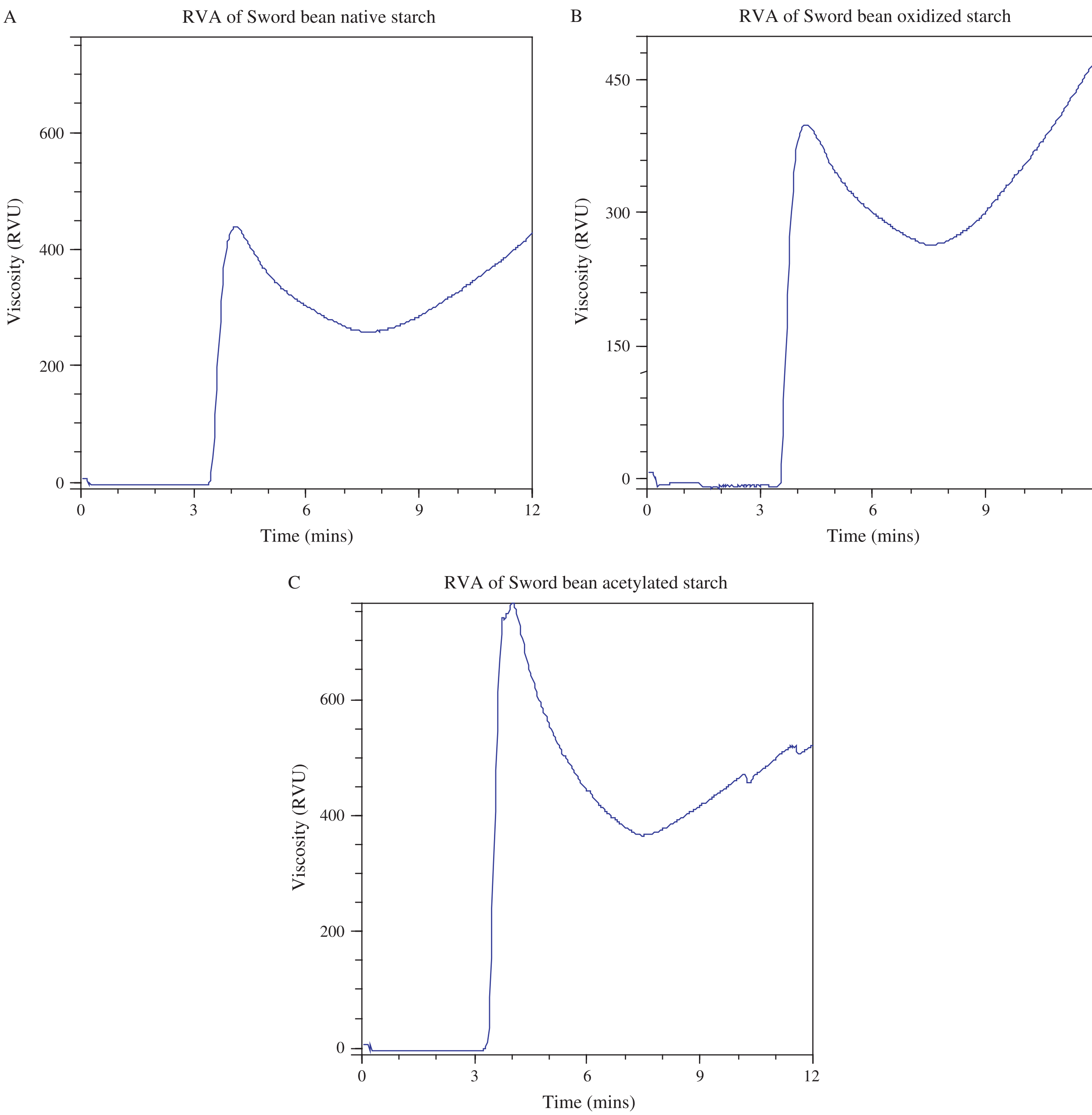

Fig. 8. (A) RVA pasting curves of Sword bean native starch. (B) RVA pasting curve of Sword bean oxidized starch. (C) RVA pasting curve of Sword bean acetylated starch.

Table 5
Thermal transition characteristics of native and chemically modified Sword bean starches (T_o, T_p, and T_c are onset, peak, and conclusion temperature, respectively).

Parameter/starch sample	Native starch	Acetylated starch	Oxidized starch
T_o (°C)	79.0	77.0	78.0
T_p (°C)	83.0	82.0	83.0
T_c (°C)	88.0	88.0	87.0
T_c-T_o (°C)	10.0	11.0	9.0
ΔH	14.0	15.0	16.0

range (64.9–80.1 °C) was broad for the acetylated and oxidized starches (Table 6). The ΔH_R values of 14.8 °C and 14.8 °C for the oxidized (SOX) and acetylated (SAC) starches respectively, is indicative of the presence of high amylose-lipid

Table 6
Retrogradation of Sword bean native and chemically modified starches

Starch	T_o (°C)	T_p (°C)	T_c (°C)	T_c-T_o (°C)	ΔH_R (J/g)
Native	64.9	71.7	78.7	3.8	3.7
Oxidized	65.3	71.8	80.1	14.8	3.4
Acetylated	65.1	71.4	79.9	14.8	3.0

T_o = Onset temperature, T_p = Peak temperature, T_c = Conclusion temperature, T_c-T_o = Retrogradation temperature range, ΔH_R = Enthalpy of retrogradation.

Table 7
Gelation capacities of Sword bean starches (on dry weight basis)

Sample	Remark	Sample concentrations (% w/v)						
		2	4	6	8	10	12	14
SBN	Gelation	+	+	+	+	+	+	+
	State	Viscous	Viscous	Viscous	Viscous	LGC	FG	FG
SAC	Gelation	−	+	+	+	+	+	+
	State	Liquid	Viscous	LGC	Gel	Gel	Gel	FG
SOX	Gelation	−	+	+	+	+	+	+
	State	Liquid	Viscous	Viscous	LGC	Gel	FG	FG

LGC; Lowest Gel Concentration, FG; Firm Gel, VFG; Very Firm Gel. SBN, Sword bean native starch; SAC, Sword bean acetylated starch; SOX, Sword bean oxidized starch.

complex, since this makes greater contribution to ΔH for the transition (Biliaderies, 1992). Also Δ*H* (measured by DSC) results more from the loss of molecular (amylopectin double-helical) order than from the loss of crystallinity (measured by X-ray crystallography) (Cooke & Gidley, 1992).

The least gelation concentration of the native, acetylated, and oxidized starches of the Sword bean is 10, 6, and 8, respectively (Table 7). The ability of starch to readily form gel when heated is a desirable quality in the food industries, although the Sword bean starch has good gelation profile, chemical modification has no appreciable effect on this properties.

4. Conclusion

Scanning electron micrograph of the starch show that acetylation and oxidation of the Sword bean starch has profound effect on the granular structure of the starch with evident of rupture of the granule. This effect was further corroborated by the result of the X-ray diffraction pattern of the Sword bean starches which changes from the Type B diffraction pattern in the native starch to Type C diffraction pattern in the acetylated and oxidized starch. Oxidation and acetylation of the Sword bean starches also enhanced the water absorption capacity of the starch. Similarly, the oxidized and acetylated starch had higher swelling and solubility profile. Other functional and physicochemical properties studied, such as pasting properties, gelatinization, retrogradation, etc., also reveal considerable changes in the properties of the modified starch, this indicate that desirable properties of the Sword bean starch can be enhanced by acetylation and oxidation for use in the food and non-food industries.

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