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IMPACT OF MICROWAVE IRRADIATION ENERGY LEVELS ON MOLECULAR ROTATION, STRUCTURAL, PHYSICO-CHEMICAL, PROXIMATE AND FUNCTIONAL PROPERTIES OF POTATO (*IPOMOEA BATATAS*) STARCH

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ABSTRACT

Starch isolated from potato was subjected to microwave treatment at different energy levels (200-800 W) to modify the functional, structural and physicochemical properties, as well as induce molecular rotation of the hydroxyl group on the starch polysaccharide. Proximate analyses revealed that moisture content reduced, while ash, protein, fat and fibre increased after modification. Fourier-transform infrared spectroscopy spectra indicated a strong shift in absorption band of OH from 3441 to 3454 cm^{-1}. Optical light microscopy revealed that starch granules were oval and spherical in shape with hyla on some of the granules. Least gelation concentration reduced following microwave treatment. Compared with the native starch, the pasting parameters of the microwave treated starches decreased, with the exception of set-back viscosity for starch modified at 800 W. Onset temperature (T_o), peak temperature (T_p) and conclusion temperature (T_c) of gelatinization increased in microwave treated starches compared with native potato starch. Also, gelatinization enthalpy increased from 8.21 J/g in native starch to 15.39, 16.36, 17.76 and 38.06 J/g in microwave treated starches at 200, 400, 600, and 800 W, respectively. It was concluded that the energy of microwave irradiation can induce and accelerate molecular rotation of the hydroxyl group on the starch polysaccharide.

Keywords: Potato starch, Microwave treatment, Molecular rotation, Physicochemical properties, Gelatinization properties

Introduction

Starch is the second largest biomass produced in nature and is considered as a major food supply for humanity (Jane, 1995). It is produced and stored in all photosynthesizing plants through their rhizomes, leaves, seeds and tubers with unique properties for each plant (Shannon *et al*., 2009, Srichuwong *et al*., 2007, Perez & Bertoft 2010). Starch sources can be primarily categorized into cereal starches, which include wheat, barley, rice and maize starches, and tuber starches, which include potato starch (Santoso, 2018). Potato starch offers considerable unique properties essential for nutrition, and is an exceptionally versatile raw material in the food, medical, cosmetic and pharmaceutical industries (Komulainen *et al.,* 2013). However, uses of

this vital biomass are always limited by some undesirable characteristics. The classical way to effectively eliminate or reduce these undesirable characteristics is by modification. In recent times, physical modifications such as superheated method, thermally inhibited treatment (dry heating), multiple deep freezing and thawing, iterated syneresis, osmotic pressure treatment, instantaneous controlled pressure drop (DIC) process, pulsed electric fields (PEF) treatment, corona electrical discharges and microwave treatment have attracted so much significance (Steeneken and Woortman, 2009; Lewandowicz and Soral-Smietana, 2004; Lim *et al*., 2002; Pkkahuta *et al.,* 2007; Szymonska *et al*., 2003; Zarguli *et al*., 2006; Maache-Rezzoug *et al.,* 2009; Han *et al.,* 2009; Nemtanu and Minea, 2006; Babu *et al*., 2018). Physical modification techniques are generally given preference as they do not involve any chemical treatment that can be harmful for human use.

Microwave activation of molecules is a typical physical method used to modify the structure and improve the functional properties of starch, with low shear than conventional heating methods (Huijie -Shen *et al.,* 2017). Microwaves are electromagnetic radiation having wavelengths ranging from one millimetre to one meter and a frequency range of 300 to 300000 MHz (Lappalainen, 2015). The frequency usually preferred in industrial, medical or scientific applications is 2.45 GHz, which corresponds to the wavelength of 12.2 cm (Lappalainen, 2015). The energy of microwaves is low, so they can only induce molecular rotation instead of having an effect on the molecular structure (Hayes, 2002; Lappalainen, 2015). Microwave heating of food does not generate an ideal thermal environment directly, but instead excites polar molecules in the reaction system to generate heat (De La Hoz, 2004). Also, microwave heating can generate an opposite temperature gradient compared with traditional heating, which results in uniform heating (Kappe, 2004). There are many advantages of microwave treatment, which include, increases process speed; achieves relatively uniform heating throughout the material; high energy efficiency; precise and rapid process control; reduces floor space requirements; obtains selective heating; and improves product quality (Mujumdar, 2007; Zhang *et al.,* 2010). There exists an abundance of literature on microwave physical modification of starch. Xie *et al*. (2013) evaluated the effect of microwave treatment on physicochemical properties of potato starch; Gómez *et al*. (2015) studied the effect of microwave treatment on physicochemical properties of maize flour; Lewandowicz *et al.* (1997) reported the effect of microwave radiation on physico-chemical properties and structure of potato and tapioca starches; Babu *et al*. (2018) prepared dual modified banana starches using cross-linking and microwave irradiation treatments; Fan *et al*. (2017) investigated the effect of microwaves on molecular arrangements in potato starch. Gao *et al.* (2019) reported the effect of dry heat, microwave and ultrasonic treatments on physicochemical properties of potato starch with or without pectin. To the best of our knowledge, no detailed information has been reported about the impact of microwave energy levels with respect to molecular rotation.

Therefore, present study was carried out to evaluate impact of microwave irradiation energy levels on molecular rotation, functional, structural and physicochemical properties of potato starch.

Experimental

Materials

Potato tubers (*Ipomoea batatas*) were purchased from Oja Oba market in Ibadan, Oyo State, Nigeria. The tubers were carefully selected to avoid rot, bruises or sign of spoilage.

Methods

Isolation and purification of starch

Potato starch was extracted using a slight modification of the method described by Adebowale *et al.* (2005). The method employed for starch isolation is outlined in Fig. 1. Potato tubers (62.5 Kg) were manually peeled, washed thoroughly and grated. The grated pulp was suspended in 5 litres of distilled water for 6 h to allow the starch to come out of the pulp. The suspended pulp was sieved using a muslin cloth with retained fibre. The fibre residue left on the muslin cloth was rewashed to remove adhering starch, after which the residue in the muslin cloth was discarded. The extracted starch was allowed to sediment for 15 h, the supernatant was decanted off and the starch was washed with 5 litres of distilled water twice to remove proteins and fibre and finally sedimented for another 15 h. The supernatant liquid was then decanted. The starch obtained was air dried on a tray for about 48 h, after which it was ground to fine powder using a mortar and pestle. It was stored in polythene bag at room temperature $(27°C)$ until use.

Potato starch yield

Starch yield (dry weight) was derived using Equation [1]:

$$\text{Starch yield\%} = \frac{\text{Weight of starch(g)}}{\text{Weight of edible portion}} \times 100 \quad [1]$$

Preparation of microwave-treated potato starches (MTPSs)

Microwave treatment method was based on the method of Ma *et al.* (2016) with slight modifications. About 100 g potato starch (PS) was suspended in 400 mL distilled water in a 1000 mL three-necked round-bottomed flask. The solution was refluxed and heated in a mono made microwave synthesizer (MAS-II, Shanghai, China) set at 60ºC for 1 h. The energy levels were set to 200, 400, 600, and 800 W to obtain four different MTPSs, namely MTPS-200, MTPS-400, MTPS-600, and MTPS-800, respectively. The untreated PS (UPS) was used as control. After 1 h, the samples were immediately cooled in an ice bath for 20 min. Afterwards, the cooled PS suspensions were filtered and air dried for 36 h. The samples were then stored in glass beakers, and sealed with a polyethylene foil for further analyses.

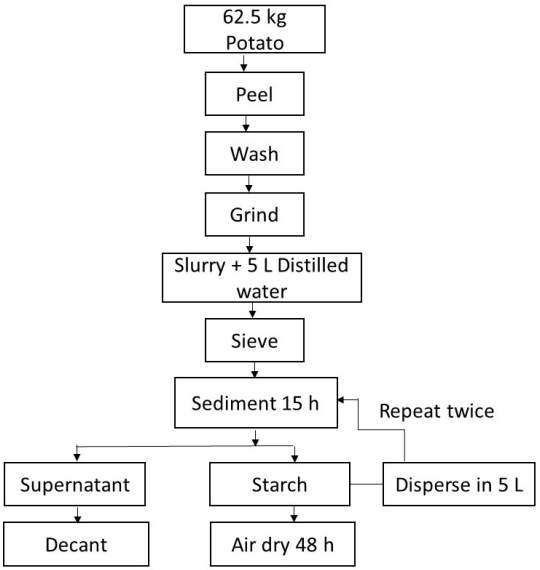

Fig. 1**:** Schematic diagram for extraction of potato starch.

Physicochemical and functional properties of starch

Proximate Analysis

Standard Association of Official Analytical Chemistry (AOAC) methods 1996, were adopted for estimating moisture content, total ash, crude protein, crude fat, crude fibre and carbohydrate. Carbohydrate (%) was calculated by difference [100 − (% moisture + % protein + % fat + % crude fibre + % ash)].

Standard optical microscopy (SOM)

Optical microscopy (magnification of 40×**)** was used to observe granule state and other physical properties of the starch granules (Han, 2011). About 1.0 mg of samples from the different energy levels was applied to a glass slide, covered with a glass slide, and fixed for observation of the granule state using standard optical microscopy equipped with 18-megapixel digital camera 18- and double-layer mechanical stage (OMAX trinocular light microscope A35140U, China).

Light transmittance measurement

Starch slurry (1% w/v) was prepared with distilled water and heated in a boiling water bath (with occasional shaking 100°C for 30 min with constant stirring according to the method of Rafiq, Singh, and Saxena (2016). The suspension was then cooled for 1 h at 30°C and the transmittance (%) of the resultant starch paste was measured at 620 nm against a distilled water blank using a UV-vis spectrophotometer (UV-1800 Shimadzu, Kyoto, Japan).

Least gelation concentration studies

The method of Coffman and Garcia, (1977) was employed with slight modification. Starch dispersions (2-14% w/v) were prepared in test tubes with distilled water (5ml), the starch suspensions were thoroughly mixed for 5 min. Then, the test tubes were heated for 30 min at 80°C in a water bath, followed by rapid cooling under running cold tap water for 2 h. Least gelation concentration was determined as lowest concentration when the sample from the inverted test tube did not fall down or slip.

Swelling power and solubility

Swelling power and solubility determination were carried out using the method of Leach *et al*. (1959). A total of 0.1 g of starch sample was accurately weighed and quantitatively transferred into a clear dried test tube and weighed (W_1). A 10 ml of distilled water was added to the test tube and the mixture was mixed thoroughly with a Whirlmix mixer for 30 s. The resultant slurries were heated at desired temperatures, ranging between 50 and 70°C for 30 min in a water bath (using temperature regulated water bath GFL, Burgwedel, Germany). The mixture was then cooled to room temperature (27°C) and centrifuged at 6000 rpm for 15 min. The residue obtained from the above experiment (after centrifugation), with the water it retained and the test tube was weighed (W_2).

$$Swelling\ of\ starch = \frac{W_2 - W_1}{Weight\ of\ starch\ (g)}$$

Aliquots (5 ml) of the supernatant obtained after centrifugation were dried to a constant weight at 110 ^{O}C using drying oven gester GT-D10 (Fujian, China). The residue obtained after drying the supernatant represented the amount of starch solubilized in water. Solubility was calculated as grams per 100 g of starch on dry weight basis.

Fourier transform infrared (FT-IR) spectroscopy

The Fourier transform infrared spectra of the PS control and MTPS samples were obtained using a Perkin-Elmer Spectrum 100 FT-IR spectrometer Walthman, (MA, USA) with an AutoIMAGE System. Each of the samples was mixed with KBr and pressed into pellets, which were then subjected to attenuated total reflectance spectroscopy in the frequency range 4000 – 400 cm^{-1}.

Pasting characteristics

The pasting characteristics of PS control and MTPS samples were determined using a Rapid Visco Analyser Super 4 model (RVA, Perten Instruments, Kurva, Sweden). But, the moisture

content of the sample was first determined to obtain the correct sample weight and amount of water required for the test. An aqueous suspension of sample was made by dispersing fifteen grams (dry basis) of starch in 25 mL distilled water. A programmed heating and cooling cycle were employed at constant shear rate, where the sample was held at 50°C for 1 min, heated to 95°C in 3 min and then held at 95°C for 2 min. It was subsequently cooled to 50°C within 3 min and then held at 50°C for 2 min. Readings were then displayed on the monitor in a numerical and graphical form and viscosities were expressed in centipoises.

Differential thermal analysis (DTA)

Thermal characteristics of PS control and MTPS samples were determined using a NETZSCH DTA 404 PC instrument (Netzsch-Gerätebau GmbH, Selb, Germany). Starch (5 mg, dry weight) was loaded into a 40 µl capacity aluminum pan and distilled water was added with the help of a Hamilton micro-syringe to achieve a starch-water suspension containing 70% water. Also, samples were hermetically sealed and allowed to stand for 2 h at room temperature $(27°C)$ before heating in the DTA. Then, the DTA analyzer was calibrated using indium (melting and and enthalpy of indium were used for temperature and heat capacity calibration, $156.6°C \ \& \ 28.44\,Jg^{-1}$) and an empty aluminum pan was used as reference. Samples were heated from 28 to 400°C at a rate of $10°C/min$. Onset temperature (T_O); peak temperature (T_p); conclusion temperature (T_C) and enthalpy of gelatinization (ΔHgel) were calculated.

Statistical analysis

Analyses were done in triplicate using fresh independently prepared samples. The results were reported as the mean value and standard deviation. The data were subjected to analysis of variance (ANOVA) using the *R*-programing language statistical software package (*R* Core Team). Duncan's multiple range test was also used to separate the significant means from the ANOVA using a significance test level of 5% ($p < 0.05$).

Results and discussion

Yield and Chemical composition of Ipomoea batatas starch samples

The purpose of percentage yield is to estimate the extractable starch in *Ipomoea batatas*. Percentage of starch obtained was 15.51 %, which is lower than 25.53 % and 30.96 % reported by Muazu et al. (2011) and Mohan et al. (2019) respectively. The moderately low starch value of 15.51 % in this present work is of significant importance in domestic and industrial food utilization (Arawande & Ashogbon 2019). The results of chemical composition of untreated and microwave treated starches of *Ipomoea batatas* are presented in Table 1. Microwave-treatment had shown to decrease the moisture content of untreated starch (12.65 %). The decrease in moisture content of all the starch samples due to microwave-treatment may be attributed to evaporation of water due to drying after treatment for 36 h. Also, the moderate range of 11.87 – 12.65% moisture recorded in this study suggests its stability against microbial activity. Babu et al. (2018) reported a reduction in moisture content of microwave irradiated banana starch. In disparity, microwave-treatment increased the values for other non-starch components such as ash, fat, fibre and protein contents. These observations are in agreement with those reported by Kemas et al. (2012) for *P. esculentus* starch except for protein content. The increments are probably related with the induction of molecular rotation (i.e., with microwave heating, the mobility of the amorphous segments could increase, leading to instability or rotation

in the molecular order of the granule) of the starch granules caused by the fact that the 1,6-linkages are located mainly in the amorphous regions of the granules, which are more susceptible to molecular rotation.

TABLE 1

Chemical composition of UPS and MTPS derivatives of Ipomoea batatas.

Starch	Parameter (%)						
	Protein	Fat	Fibre	Ash	Moisture	Carbohydr.	Dry matter
UPS	1.29±0.06^{a}	0.18±0.01^{a}	0.57±0.01^{a}	0.72±0.04^{a}	12.65±0.04^{a}	84.59±0.06^{a}	87.35±0.01^{a}
MTPS-200	2.37±0.08^{b}	1.21±0.01^{b}	1.49±0.05^{b}	1.68±0.05^{b}	11.87±0.04^{b}	81.38±0.07^{b}	88.13±0.05^{a}
MTPS-400	1.78±0.02^{b}	1.13±0.03^{c}	1.28±0.03^{b}	1.49±0.01^{c}	12.09±0.02^{b}	82.23±0.04^{b}	87.91±0.03^{a}
MTPS-600	1.69±0.01^{b}	1.07±0.01^{b}	1.22±0.05^{d}	1.54±0.03^{b}	11.96±0.01^{c}	82.52±0.03^{b}	88.04±0.02^{a}
MTPS-800	1.38±0.02^{c}	0.86±0.03^{bc}	1.35±0.03^{b}	1.42±0.01^{b}	12.38±0.02^{e}	82.61±0.04^{b}	87.62±0.03^{a}

All values are means of triplicate determinations ± standard deviation. Means within columns with different superscripts (a, b, c, d, e) are significantly different, LSD ($P < 0.05$). UPS: Untreated potato starch; MTPS: Microwave treated potato starch at different energy levels; MTPS-200, MTPS-400, MTPS-600, and MTPS-800; Carbohydr: Carbohydrate.

Optic microscopy

The impact of microwave-treatment on *Ipomoea batatas* starch granules was investigated using standard optical microscopy. The micrographs of untreated and microwave-treated starch granules are shown in Fig. 2. The untreated potato starch (UPS) granules were observed to be mostly oval, spherical in shape with a smooth surface and non-dappled edges which are typical characteristics of potato starch. As observed, after microwave-treatment at different energy levels (200, 400, 600 and 800 W), the conditions of treatment significantly altered and truncated the granular structure of the potato starch. In the starch modified at 200 W, presence of hyla on some of the starch granules was observed with different shapes. They appear as crack/groove on the starch granules (Sarkar, 2016), which are due to internal cracking during microwave-treatment of the starch. These results agreed with the earlier report on jack bean starch (Lawal & Adebowale, 2005). Further increasing the energy level to 400, 600 and 800 W, the starch granules appear distinctly broken and wrinkled with uneven edges, which means that the microwave energy vibrates the water molecules present in the crystalline regions of the starch granules thereby destroying the lamellar arrangement of the amylopectin crystals and disorientating the helical structures of the amylose (Palav & Seetharama, 2007). Furthermore, it is worth noting that granule swelling occurs at all the three higher energy levels, and the oval shape completely disappeared. This observation is consistent with previous report on effect of heating rate on starch granule morphology and size (Patel & Seetharaman, 2006).

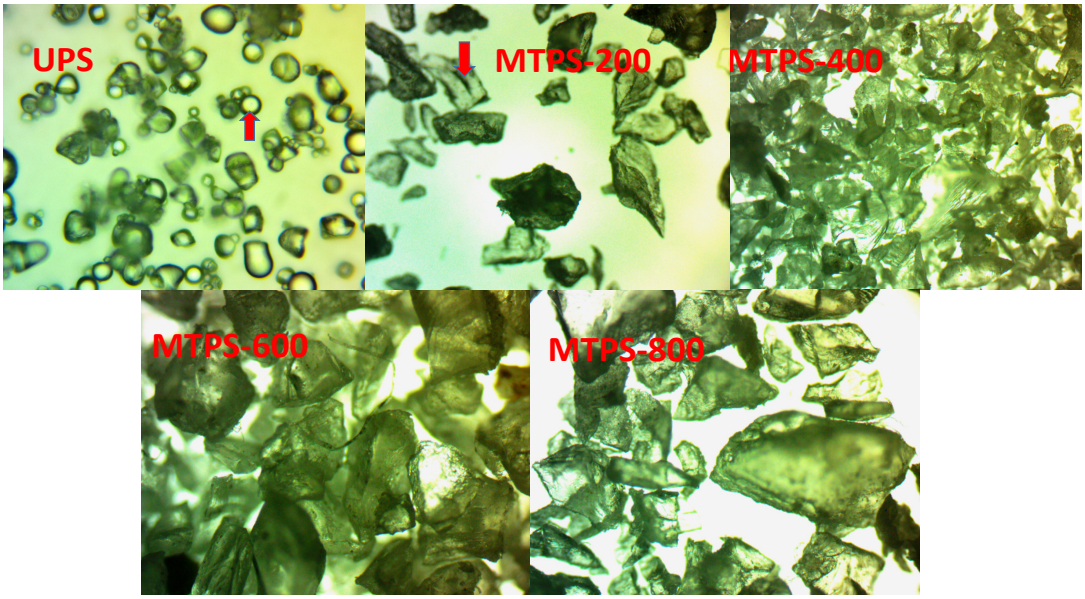

Fig. 2: Granule morphology of UPS (control), MTPS-200, MTPS-400, MTPS-600 and MTPS-800 using the technique of 40× standard optical light microscopy.

Light transmittance (Transparency)

Light transmittance is one of the key parameters in starch paste dispersion chemistry. The light transmittance results of the untreated and microwave-treated starches at different energy levels obtained in this study are shown on Fig. 3. It can be observed that microwave-treatment significantly decreased the light transmittance of untreated/native starch. The lowest transparency value (which is the highest opacity value) was observed in MTPS-200 (33.5%), whilst the smallest decrease was observed in MTPS-600 (46.7%) compared with the control. The decrease in transparency observed in microwave-treated starches might be due to the gelatinization of the granules as a function of the vibrational motion of the polar molecule during microwave treatment. For MTPS-400, MTPS-600 and MTPS-800 starches, only slight transparency increases were observed relative to MTPS-200 starch. The increase in transparency after microwave treatment above 200 energy level could be the development of a network relating to those chains leached from the starch granules during the microwave treatment (Xie *et al*., 2013). Overall, all the microwave-treated starches exhibited transparency in the range of 33.5 to 46.7% (< 50%), this observation is likely due to the impact of the energy levels and formation of less fragile granule remnants, which lowered the capacity of the starch paste to transmit light, thereby decreasing the transparency of potato starch. This result was in agreement with Hu *et al*. (2018) who reported that the superheated steam treatment significantly decreased transparency of potato starch.

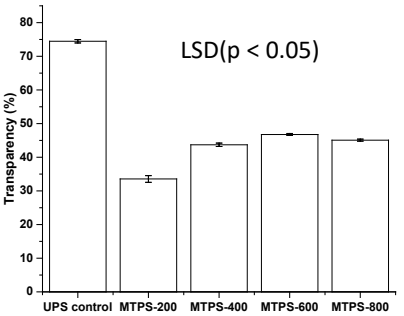

Fig. 3: Transparency of UPS (control), MTPS-200, MTPS-400, MTPS-600 and MTPS-800. The error bars represent the standard deviations of means.

Gelation properties

Gelation properties of the starches are presented in Table 2. Gelation is a phase phenomenon resulting from aggregation of starch molecules. Least gelation concentration (LGC) is the ability of starch to form gel which provide structural matrix for holding water and other water-soluble materials like sugars and flavors (Shad *et al*. 2013). According to Sathe *et al.,* (1982), LGC varies for different starches depending on the relative ratios of their structural constituents like proteins, carbohydrates and lipids. The result obtained in this study indicates that all the starches were not able to form gel at low concentrations (< 8%), but LGC of the starch decreased following microwave treatment. Reduction in LGC value is an indication of better gelating properties. In the present study, the reduction after microwave treatment may be due to the disruption of crystalline structure induced by microwave radiation (Lewicka *et al*., 2015). That is, disruption in the amylopectin structure aided amylopectin retrogradation, thus resulting in a higher gel strength. Both MTPS-400 and MTPS-600 had LGC value of 8%w/v, but at 4%w/v concentration, MTPS-600 appeared viscous while MTPS-400 remained a liquid. Overall, these observations suggest that the microwave-treated starch could have better gelating properties than the untreated starch and may be useful as a thickening and gelling agent in food products such as sauce and puddings.

TABLE 2

Gelation properties of UPS and microwave-treated starches.

Concentration (% w/v)	Starch sample				
	UPS	**MTPS-200**	**MTPS-400**	**MTPS-600**	**MTPS-800**
2	−Liquid	−Liquid	−Liquid	−Liquid	−Liquid
4	−Liquid	−Liquid	−Liquid	−Viscous	−Viscous
6	−Liquid	−Liquid	−Viscous	−Viscous	−Viscous
8	−Liquid	−Viscous	+Gel	+Gel	−Viscous
10	−Liquid	−Viscous	+Gel	+Firm gel	+Gel
12	−Viscous	+Gel	+Firm gel	+Firm gel	+Firm gel
14	+Gel	+Gel	+Gel	+Firm gel	+Firm gel
LGC[a]	14	12	8	8	10

[a]Least gelation concentration.

Swelling power and solubility

Swelling power and solubility of starches were observed to be a function of temperature between 50 – 70^{O}C as indicated in Figs. 4 and 5. The results indicate that both swelling power and solubility decreased significantly with increase in temperature but modification increased the swelling power and decreased the solubility (Figs. 4 and 5). Swelling power occurs due to the non-covalent bond between

starch molecules. The solubility of microwave-treated starches was lower in all cases as compared to untreated starch. The reduction in solubility following microwave treatment observed in this study is in consonance with those reported by Luo *et al.* (2006). Among the microwave-treated starches, the largest swelling capacity was obtained for MTPS-800 (12.9 g/g) at 50^{O}C which is higher than 7.7 and 6.73 g/g of same starch at 60 and 70^{O}C, respectively. Generally, starch gives high swelling power values, suggesting that they are useful in food systems where swelling is required. The swelling power values obtained in this work were in contrast to those reported by Adebowale *et al*., 2002 for bambarra groundnut; Lawal & Adebowale, 2005 for jack bean; Lawal *et al*., 2005 for hybrid maize and Nadiah *et al*., 2015 for potato starches but consistent with previous reports on swelling of red sorghum starch (Adebowale *et al*., 2005) and acid thinned sorghum starch (Singh *et al*., 2009). The result also showed that the solubility pattern of all the starches decreased with increasing degree of temperature. The maximum solubility of untreated starch was observed at 50^{O}C with solubility index of 2.4%, while all the microwave-treated starch derivatives had maximum solubility at the same temperature with solubility index in the range of 2.1 to 0.9 %. This decrease in solubility due to both microwave treatment and increase in temperature can be attributed to the decreased in hydrophilicity of the starch. A similar trend of change was reported by Babu *et al*., 2018 for banana starch.

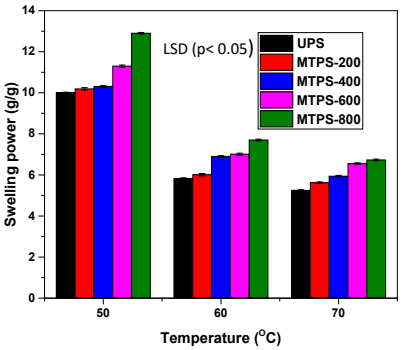

Fig. 4: Effect of temperature on swelling power of untreated and microwave treated starch of *Ipomoea batatas.* Error bars: standard deviations; results are means of triplicate determinations.

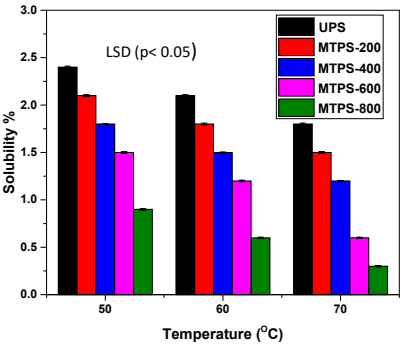

Fig. 5: Effect of temperature on solubility of untreated and microwave treated starch of *Ipomoea batatas.* Error bars: standard deviations; results are means of triplicate determinations.

Pasting properties

Pasting properties of untreated and a representative of microwave-treated starches measured using RVA are presented in Fig. 6, and their pasting parameters are given in Table 3. In general, the pasting temperature of the microwave-treated starches increased significantly from control starch (UPS). Increment in pasting temperature after microwave treatment was consistent with most of the other starches such as lentil, potato and yam starches reported by Hoover and Vasanthan (1994). In the microwave treated samples for MTPS-200, MTPS-400, and MTPS-600, the peak viscosity, trough viscosity, final viscosity, breakdown viscosity and setback were significantly decreased with increase in the energy level, but higher power or energy level (MTPS-800) induced the opposite trend and an increase in all the pasting parameters relative to other treated starches was observed. It is also noteworthy that MTPS-800 starch had higher setback value (1789 cP) compared with control starch (911 cP), which reflected the degrees of recrystallization at higher energy level. This observation is strengthened by the report of Lawal *et al.* (2005). Furthermore, the peak viscosity of the starch decreased upon treatment by 80% (from 5988 to 1196 cP) for MTPS-200, 82% for MTPS-400, 88% for MTPS-600 and 68% for MTPS-800, indicating reduced swelling power of the starch granules which improves the shear stability of the granules leading to higher setback.

The final viscosity values ranged from 892 to 4901 cP with the lowest value observed in MTPS-600 starch and the highest found in UPS control starch. Moreover, the breakdown values ranged from 14.5 to 1998 cP. The lower the breakdown, the higher the ability of the sample to withstand heating and shear stress during cooking of starch. From this research, MTPS-600 had the lowest breakdown value (14.5), and thus had the predominant ability to withstand heating during cooking. Microwave treatment of rice grain has also been reported by Pinkrová et al. (2003) to decrease the peak viscosity over the native starch.

TABLE 3

Pasting characteristics of UPS and microwave-treated (MTPSs) starches.

Parameter	Starch sample				
	UPS	**MTPS-200**	**MTPS-400**	**MTPS-600**	**MTPS-800**
PV (cP)	5988	1196	1085.5	718.5	1894
TV (cP)	3990	1096	1014	704	1578
BV (cP)	1998	100	71.5	14.5	316
FV (cP)	4901	1852	1556	892	3367
SV (cP)	911	756	542	188	1789
P_{Temp} (°C)	75.05	77.52	79.56	81.60	83.9

PV, Peak viscosity; TV, trough viscosity; BV, breakdown viscosity; FV, final viscosity; SV, setback viscosity; P_{Temp}, pasting temperature.

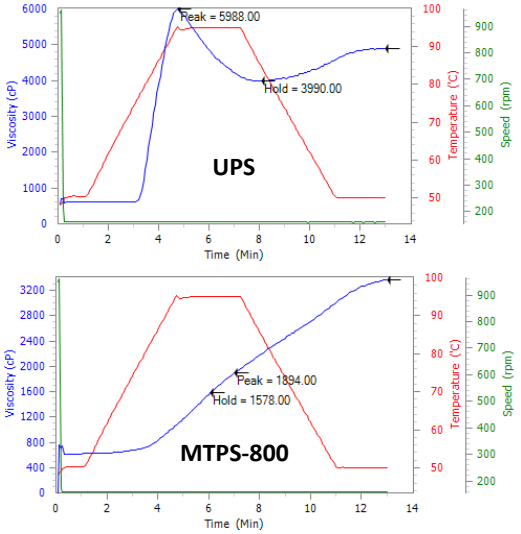

Fig. 6**:** Rapid visco analyzer pasting patterns of UPS and a representative of microwave-treated starches (MTPS-800).

Fourier transformation infrared spectroscopy analysis

The FT-IR spectra were used to probe the change in the molecular rotation and structure after the microwave treatment of control starch, and the results are presented in Fig. 7. The chemical structure and compositions of starch have been established to have strong absorption band in the range of 3700-3000 cm^{-1} resulting from O–H stretching vibration (Pozo *et al.,* 2018). The broad band observed at 3441 cm^{-1} in the control sample (UPS) confirmed the presence of O–H vibrations. Compared with MTPSs, the characteristic band at 3441 cm^{-1} in the UPS shifted to a higher wavelength (3454 cm^{-1}), indicating inducement of molecular rotation and excessive chain mobility of O–H group, thus the hydrogen bonds between starch molecular chains in the MTPSs were stronger. This observation suggests that when starch molecule is subjected to microwave irradiation, the O–H group in the three-dimensional micellar networks in the granule can be rotated. Similar shift to a shorter wavelength has been reported for starch nanoparticles by Qin *et al*. (2016). All starches exhibited a well-defined band around 1018 cm^{-1}, which was assigned to the vibration of C–O–H deformation and has been used to express the amorphous component of starch (Ferreira-Villadiego *et al*., 2018). However, a sharp decrease (about 39% decrease) in peak intensities of the band at 1018 cm^{-1} was found in all the MTPSs, suggesting an increase in the ordered structure of starches. Moreover, an absorption band in the range of 2933-2928 cm^{-1} was seen in all the samples (control and treated), and can be attributed to the asymmetric stretching of C-H from glucose. In addition, all spectra show vibrational modes at low wavenumbers (below 800 cm^{-1}), which was attributable to the skeletal mode vibrations of the glucose pyranose ring (Kizil *et al*., 2002). This observation is in agreement with the previous research on investigation of the glycosidic linkages in several oligosaccharides using FT-IR and FT-Raman spectroscopies reported by Sekkal *et al.* (1995).

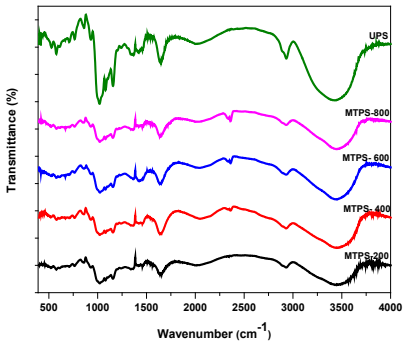

Fig. 7: FTIR spectra of control starch (UPS) and microwave-treated starches.

Thermal properties of starch

DTA measures and records the amount of heat involved in the starch gelatinization. Gelatinization is an important property of starch which occurs through the collapse of molecular order during the heating process. Fig.8 presents the gelatinization endotherms of control and microwave treated starches, and their thermal parameters are summarized in Table 4. The results indicate that gelatinization enthalpy (ΔH) increased from 8.21 J/g in control starch to 15.39, 16.36, 17.76 and 38.06 J/g in MTPS-200, MTPS-400, MTPS-600 and MTPS-800, respectively. It was also observed that enthalpy of gelatinization was significantly higher for MTPS-800 (38.06 J/g) compared to other MTPSs. Factor such as degree of crystallinity has been reported to be one of the factors that affect gelatinization enthalpy values (Cai *et al*., 2015). Gelatinization enthalpy of starch granules is associated with the energy required for breaking of double helices (Tester *et al*., 2004). Due to the further degradation of amorphous regions, which also caused an increase in the percentage crystallinity, it was required more energy (ΔH from 8.21 J/g to 38.06 J/g) to melt the potato starch granules (Garcia *et al*., 2015).

Microwave treatment revealed significant increase in the onset temperature (T_O), peak temperature (T_P), and concluding temperature (T_C). This observation is in agreement with those reported by Lewandowicz *et al.* (2000). T_O, T_P and T_C shifted to higher values in MTPSs compared to control starch. The highest T_O, T_P and T_C of 92.1, 121.1 and 160.3^{O}C, respectively, were observed for MTPS-800 starch. The high gelatinization temperature for MTPS-800 starch indicates that more energy is required to initiate starch gelatinization. In addition, the gelatinization temperature ranges ($T_C - T_O$) of MTPSs at different energy levels were all significantly lower than control starch. These results further indicated that the thermal transitions were not sharp, which can be explained by the low heating rate employed (Hohne *et al*., 2003). In general, the thermal characterization of starch is important because this polysaccharide is surrendered to several thermal transformation processes in industry.

TABLE 4

DTA parameters of control and microwave-treated starches.

Samples	T_O (^{O}C)	T_p (^{O}C)	T_C (^{O}C)	$T_C - T_O$ (^{O}C)	ΔH (J/g)
UPS	79.7	111.9	150.1	70.4	8.21
MTPS-200	91.7	117.4	159.4	67.7	15.39
MTPS-400	91.2	118.2	158.2	67.0	16.36
MTPS-600	90.2	119.8	156.1	65.9	17.76
MTPS-800	92.3	121.1	160.3	68.0	38.06

T_o: onset temperature; T_p: peak temperature; T_c: conclusion temperature; $T_c - T_o$: gelatinization temperature range and ΔH: gelatinization enthalpy

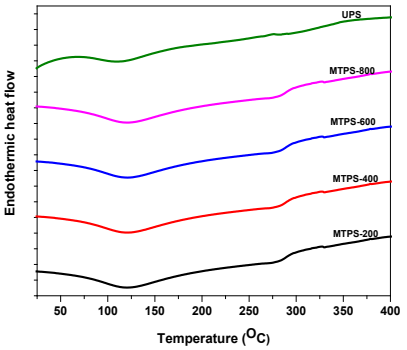

Fig. 8: DTA gelatinization thermograms of control (UPS) and microwave-treated (MTPSs) starches.

Conclusion

Microwave irradiation treatment could effectively modify the functional, structural and physicochemical properties, as well as induce molecular rotation of the hydroxyl group on the starch polysaccharide. Microwave treatment activated notable changes in the structure of potato starch morphology. Control starch granules displayed an oval shape with a smooth surface and non-dappled edges. Hyla and fractures with uneven edges appeared when granules were subjected to microwave treatment. Microwave treatment reduced the transparency of the native starch. Gelation properties of the control starch improved following microwave treatment. Swelling power and solubility decreased as the temperature increased. Microwave modification increased the swelling power but decreased the solubility pattern of the control starch. Modification promotes breakage of starch chains in amorphous regions, resulting in reduced PV, TV, BV, SV and FV and thus becoming materials more suitable for the formation of variety of food products due to low viscosity. The FTIR spectroscopy showed that the characteristic absorption band of OH in the control sample shifted to a higher wavelength after microwave irradiation. DTA data showed that the enthalpy of gelatinization increased following microwave irradiation.

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Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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