J Food Sci Technol (January 2022) 59(1):344–354
https://doi.org/10.1007/s13197-021-05020-9

ORIGINAL ARTICLE

Application of microwave and hydrothermal treatments for modification of cassava starch of Manipur region, India and development of cookies

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Revised: 20 January 2021 / Accepted: 1 February 2021 / Published online: 15 February 2021

Abstract The cassava (*Manihot esculenta*) root provides sustainable cheap source of starch that can be modified using microwave and hydrothermal treatments. The modified starch is of great demand in the market for its varied food applications. The microwave modified wet milling dry chips starch, microwave modified pulp starch (MD-PS), microwave modified dry chips starch were the microwave treated starch obtained from starches of pulp starch (PS), wet milling dry chips starch and dry milling dry chips starch, respectively. On the other hand, by using hydrothermal treatment followed by freeze-drying in PS gave autoclave freeze-dried 10% PS (AF-10PS), autoclave freeze-dried 20% PS (AF-20PS). The physicochemical and functional properties of the samples were investigated. The calorific value of modified starch was found to be 341–358 kcal/100 g. The microwave-modified starch lowered true densities as compared to hydrothermal treated starch. FT-IR spectra of microwave-modified starch confirmed six prominent peaks between 4500–500 cm^{-1}. Thermal treatment affected the digestibility and found lower digestion resistibility in modified starch compared to native starch. The structures of the starch granules were more enzymatically susceptible in hydrothermally modified starch. The microwave-modified starch resulted higher resistant starch as compared to hydrothermally modified starch. The cookies quality using MD-PS was checked by developing with 10–40% level of substitution of wheat flour. Overall cookies acceptability was found above sensory score 5. This study will help to provide functional ingredients that serve health benefit beyond nutrition.

Keywords Modified-starch · Cassava · Starch · Microwave modification

Introduction

Cassava (*Manihot esculenta*) is one of the under-utilized root crops of Manipur Region of India. The cassava root is well known for its vast reserve source of starch. The occurrence of starch in abundant quantity renders it favorable for various industrial uses, wherein starch modification can be carried out chemically or physically by modifying its structure and physicochemical properties. Raw starches have limited application and it does not meet the functional characteristics demand by manufacturers (Obadi and Xu 2021). The starch modification can be exploited for beneficial applications. Food manufacturing industries generally use modified starch to enhance functional properties like pasting properties (for paste consistency, smoothness, and clarity) and increase ability to withstand low temperature, favorable to impart freeze–thaw and cold storage stabilities (Wu and Seib 1990). The starch granules generally appear in various shapes and sizes with different physicochemical and functional characteristics (Tharanathan 1995). With the increase in the health-conscious diet, the incorporation of dietary starch in food has gained importance as it is considered a good replacement for dietary fat. The present ongoing research worldwide indicates that, there will be an ever-increasing industrial demand for modified starches. The modified starch is sustainable to produce by using an inexpensive, safe, and economically viable method. The modified starch

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can provide functional characteristics into a desirable way (Obadi and Xu 2021). The physical method proved to be a good alternative to chemical-based modifications. It is also possible to modify the starch properties by simple physical methods like hydrothermal or steam-pressure treatments (Moorthy 2002). Sustainable, simple and green starch modification approach is widely accepted and sought by researchers. The heat-moisture treatment (HMT) is a simple and sustainable technique; it could alter the starch granules morphology, sizes, and its crystallinity in case of cereal starch (Wang and Zheng 2021). HMT increase crystallinities and enthalpies of debranched waxy maize starch (DWMS) (Chang et al. 2020).The changing degree depends on the HMT parameters and the plant botanical origin (Wang and Zheng 2021). Therefore, the microwave method becomes a novel way of starch modification technique. When the moisture content of starch is above 20%, it is observed that an isothermal phase is visible before the rise of temperature (Lu and Yang 2006). The modified starch increases the content of slowly digestible starch (SDS) and resistant starch (RS) (Chen et al. 2017). It also helps to avoid the crystallinity with the decrease of the viscosities paste, increased gel transparency and the water solubility of starch (Colman et al. 2014). These are complicated and time-consuming methods. (Liu et al. 1999). However, there is always concern of safety-use of chemicals when associated with food products. The present investigation was carried out in the backdrop of ever-increasing demand of modified starch in the market using sustainable raw materials and techniques i.e. physical modification methods, which can be considered very safer as compared to chemical modification.

Materials and methods

Extraction of starch

Isolated pulp starch (PS), wet milling dry chips starch (WCS), wet milling fermented starch (WFS), dry milling dry chips starch (DCS) and dry milling fermented starches (DFS) were taken for starch modification. The starch extraction and modification step is illustrated in Fig. 1.

Starch modification-using microwave

The domestic microwave oven (Make LG, Model MH-3948) was used for microwave treatment.

Moisture equilibration of starch

The moisture content of cassava starch was adjusted to 20% and it was equilibrated at 4 °C for 4 days with intermittent mixing.

The starch sample with 20% moisture content was given microwave heated treatment at 900 W for 30 min. After every 2 min, the sample was stirred to mix and heat uniformly. After microwave treatment, the sample was kept for 30 min in desiccator and oven-dried at 45 ± 1 °C and pulverized and kept in airtight container for further analysis (Zhang et al. 2009).

Starch modification using autoclave

Cassava starch was suspended into distilled water maintaining at 10% and 20% (w/v). It was autoclaved (Make HMG India; Model Laboratory Model)for 30 min at 120 ± 1 °C using 15 psi and stored for 24 h at 4 °C and repeated the autoclaving and cooling cycles for 3 days. After final autoclave treatment, the sample was freeze-dried. The final dried sample was pulverized into fine powder and stored in air tight container for further analyses (Klein et al. 2013).

Pectin yield

Pectin extraction and determination

The pectin extraction was done following the method of Prakash et al. (2013) with slight modification. One g of modified starch was mixed with 16.9 ml of distilled water into 250 ml pyrex beaker. The pH of the mixture was maintained at 1.4 using 16 mM/L sulphuric acid. The obtained solution was treated in microwave at power 360 W with irradiation time 180 s. After microwaved treatment, it was kept outside to cool down until it reached room temperature and filtered using Whatman No. 1 filter paper and to an equal volume of filtrate, 95% ethanol was added (v/v). The final solution was kept for 1.5 h and the wet residue obtained was washed with 95% ethanol (v/v) 3 times (Li et al. 2012).

The pectin-wet residue was dried in a hot air oven at 50 ± 1 °C until it maintained a constant weight. The pectin yield (PY) was determined using (Li et al. 2012) and (Prakash et al. 2013) methods.

$$\text{Pectin yield(PY\%)} = \frac{\text{Dried pectin weight}}{\text{Dried modified starch weight}} \times 100$$

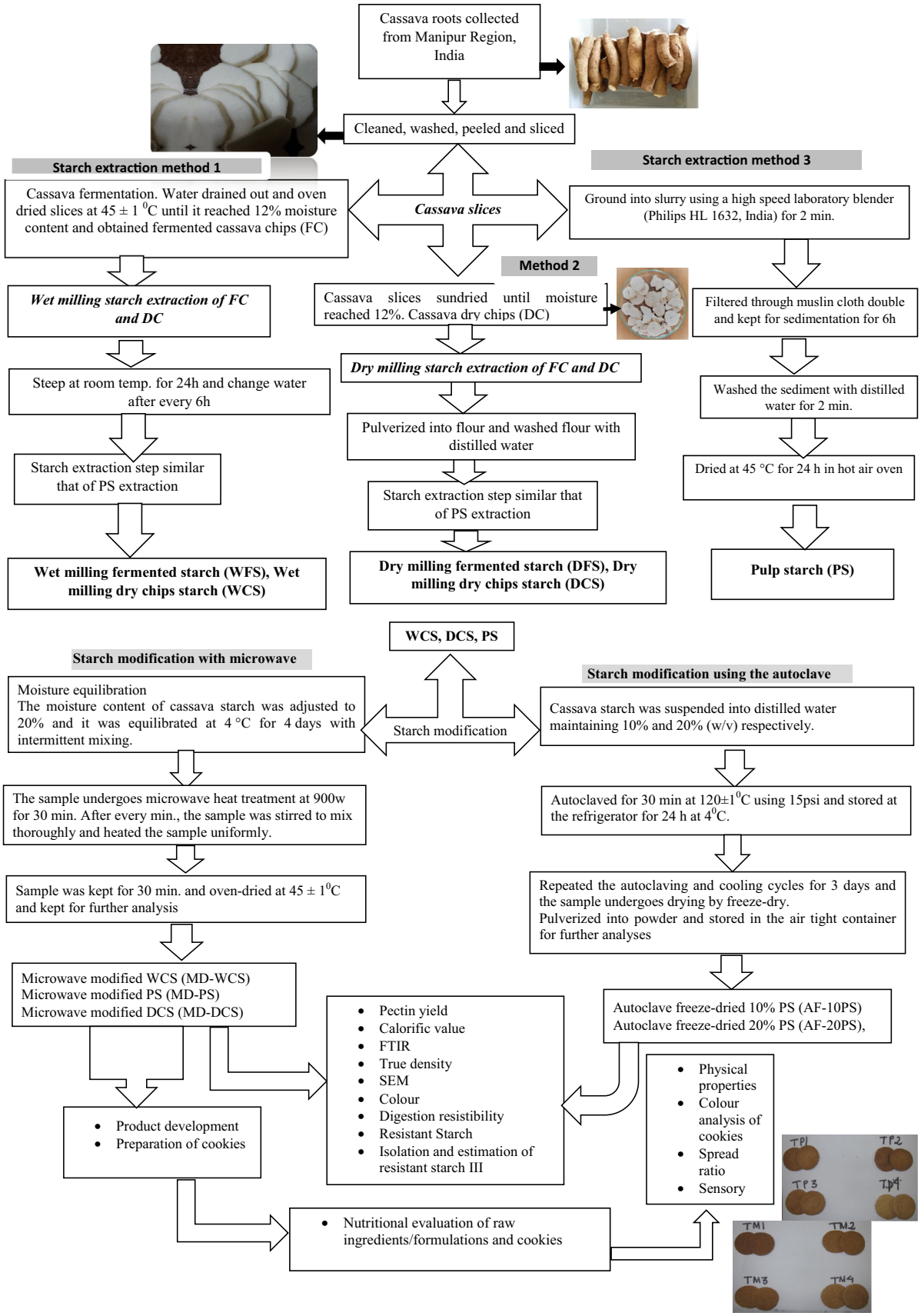

Fig.1 Flow chart of cassava starch modification and development of product

Estimation of calorific value

The calorific value of the sample was measured using auto bomb calorimeter (Make: Changsha Kaiyuan Instrument Co. Ltd; Model: 5E–1AC/ML) Doyle et al. 2007).

Fourier transform infrared spectroscopy (FT-IR) spectra of modified starch

Fourier transform infrared spectrometer (Nicolet, USA, Impact 410, Omnic E.S.P.5.0) was used to find out the spectra of the starch samples. It was fitted with KBr optics and DTGS (deuterated triglycine sulfate) was used as the detector and the resolution range for the spectra was recorded from 400–4000 cm^{-1} (mid-infra-red zone) with a resolution of 4 cm^{-1}. The modified starchample: KBr was in the ratio 1:4 (w/w) and was thoroughly mixed and pressed to form the pellet. This pellet was used for the analysis in the spectrometer. The background value of pure KBr was known before scanning of each sample.

True density

An automated gas pycnometer (Porous Materials, Inc.; Model PYC-100A,) was used to determine particle true density of modified cassava starch. The analysis was carried out using the known quantity of starch sample by filling in a 10 cc capacity graduated cylinder. The cylinder was placed in the automated gas pycnometer system and measured its true density Ashogbon and Akintayo 2012).

Morphological study

The morphological study of the modified starch sample was carried out using a scanning electron microscope (Make: JEOL, JAPAN, Model: JSM 6390LV, Software: JEOL SOFTWARE window-based) and scanning electron microscopy-energy dispersive X-ray analysis (SEM EDX) (Make Oxford Instrument, INCA X sight; Model 7582). The samples were kept into the airtight enclosure, which fitted perfectly into microscope stud using a sputter gold coat. The power supply was 20 kV with magnifying power 1500X.

Color

Colorimeter (Ultrascan VIS, Hunterlab, USA) was used for the color analysis of modified cassava starch (Hunter et al. 1987; CIE 1971; 1978).

Digestion resistibility

The digestion resistibility (DS) of starch samples was determined by Zhu et al. (2011) method with slight modifications. Starch sample (500 mg, dry basis) was treated with 15 ml sodium phosphate buffer (0.15 M, pH 6.5) in a centrifuge tube. Each sample was divided into two parts one for the heat treatment method and the other for the non-heat treatment method. The thermal heat treatment was done in a preheated boiling bath for 20 min. To each tube 30 mg pancreatin (RM7348-100G, HiMedia Laboratories Pvt. Ltd. Mumbai, India) and 30 mg gelatin (10,010,328, Sinopharm Chemical Reagent Co., Ltd., P.R. China) was added. The samples were incubated in a shaking water bath (Make EquitronMedica Private Limited; Model#8406)at 37 °C, 170 rpm for 6 h. Sulfuric acid (1.0%, w/v) 15 ml was added to stop hydrolysis and was centrifuged (Make Eppendorf®; Model 5430/5430R) at 20,000 × g for 10 min. The residue was washed with 15 ml of 80% ethanol (v/v) and then centrifuged at 20,000 × g for 5 min. The final residue was oven-dried at 105 ± 1 °C 24 h. The digestion resistibility calculated using the following equation

$$\text{Digestion resistibilty(DS\%)} = 100 - \left\{ \left(\frac{\text{Sample weight - Dried sample residue weight}}{\text{sample weight}} \right) \times 100 \right\}$$

Resistant starch

Isolation and estimation of resistant starch

The starch sample of 0.4 g (dry weight basis) was taken in a polypropylene centrifuge tube. The weight of the centrifuge tube was recorded. The phosphate buffer (pH 6.0, 55.6 mM) was added to the centrifuge tube followed by 0.16 g α-amylase (HIMEDIA, GRM638-100G). The mixture was incubated for 16 h at 37 °C. The sample was brought to room temperature. The pH of the mixture was adjusted to 4.5 using phosphoric acid solution 2 ml/100 ml (v/v). Amyloglucosidase (0.4 ml)was added and incubated for 30 min at 60 °C. It was centrifuged (Make Eppendorf®; Model 5430/5430R) for 15 min at 4500 × g. The supernatant was decanted and the residue was washed with

phosphate buffer two times. The final residue re-suspended with 20 ml of phosphate buffer (pH 7.5, 0.08 M). Protease (0.4 ml) was further added to it and incubated at 42 °C for 4 h. Finally, it was centrifuged for 6500 × g for 15 min. The precipitate was washed with distilled water and then dried in a hot air oven at 60 °C until it reached the constant weight. The residue after digestion was considered as RS III and its value was expressed on a dry matter basis (Eerlingen et al.1993).

Product development

Preparation of cookies

The cookies were prepared using the ingredients listed in Table 1. The cookies prepared using whole-wheat flour and pulp starch (PS) were considered as a control sample (TP). The cookies prepared from whole-wheat flour with modified cassava starch (MD-PS) were taken as the experimental sample TM1 (10% substitution level), TM2 (20% substitution level), TM3 (30% substitution level), TM4 (40% substitution level). Both experimental and control cookies substitute wheat flour by modified starch at the level of 10–40%, respectively. Distilled water (28 ml) was used for dough preparation and the moisture content of the dough was 21.44%. The baking powder was mixed with composite flour and passed through a sieve to get uniform flour mixture. The sugar powder along with butter was whisked together until it formed a soft texture. The dough was prepared and rolled out into flat and molded into a small circular shape. The molded cookies were placed into baking trays for baking. The baking oven was pre-heated for 10 min and baked for 18 min at 180 ± 2 °C. The final product was kept to cool down until it reached room temperature. It was stored in LDPE zipper pouches at room temperature (27 ± 2 °C) for further investigation.

Nutritional values of raw ingredients/formulations and cookies

The nutritional values of raw ingredients (wheat flour, sugar powder, butter or oil, baking powder) which includes energy (kcal), protein(g), carbohydrate (g), fat (g), dietary fiber (g) per 100 g and Ca (mg/100 mg) were noted from packaged nutritional information as listed down in Table 2. The nutritional contents of cassava starch (both native and modified starch) including PS, MD-PS were also determined.

Physical properties

Colour analysis of cookies

The color value of the samples was analyzed using colorimeter (Ultrascan VIS, Hunterlab, USA) (Hunter et al. 1987; CIE 1971; 1978).

Sensory evaluation of cookies

After taking out the cookies from oven, allowed to reach normal temperature and was followed a sensory evaluation by 25 semi-trained panelists. The parameters included taste, texture, appearance, aroma, and overall acceptability were conducted by using a nine-point hedonic scale ranging from 1–9 which started from dislike extremely to like extremely. The overall acceptability means score achieved above 5 was considered as an acceptable product (Lazaridou et al. 2007).

Statistical analysis

Physicochemical characteristics, pasting and thermal properties of cassava starch analysis were done in triplicate and data were presented as means ± SD. The graph shown in the figure was statistically analyzed using Origin 8.0.

Result and discussion

Pectin yield

The pectin yield of modified cassava starch is shown in Table 3. It was observed the highest pectin yield of 14.24 ± 0.01% in MD-WCS. However, AF-10PS, MD-PS revealed close pectin yield and lower value in AF-20PS. The extraction of pectin from the conventional technique is time consuming and complicated, while the application of microwave-assisted extraction (MAE) is convenient to carry out at the shorter time with accuracy, with less solvent, higher extraction rate, and improved quality products (Bailoni et al. 2005). The findings showed that the effect on pectin yield could be seen in WCS and PS derived modified starch. The pectin content found higher in citrus fruits but lower in the case of cassava. The study conducted by Bailoni et al. (2005) reported that cassava meal contained 38.2% pectin as protopectin. Literature revealed that the legumes and tubers found higher pectin (13.2 ± 8.4 g/kg DM) than that of cereals (2.8 ± 0.5 g/kg DM) (Bailoni et al. 2005).

Table 1 Physicochemical characteristics, color, bulk density of MD-WCS, MD-PS, AF-WCS, AF-20PS, AF-10PS*

	Analysis	MD-WCS		MD-PS		AF-WCS		AF-20PS		AF-10PS	
Physicochemical characteristics (g/100 g dwb)	Calories (kcal/100 g)	357.58 ± 0.34	357.50 ± 0.34	341.17 ± 0.47	352.36 ± 0.56	345.65 ± 0.75					
	Resistant starch (%)	61.62 ± 0.53	57.17 ± 0.31	8.14 ± 0.12	8.7 ± 0.16	10.51 ± 0.14					
	Pectin yield (%)	34.24 ± 0.34	1.84 ± 0.45	ND	0.56 ± 0.37					1.14 ± 0.32	
	Digestion resistibility	Heat-treated (%)	Non-heat treated (%)	Heat-treated (%)	Non-heat treated (%)	Heat-treated (%)	Non-heat treated (%)	Heat-treated (%)	Non-heat treated (%)	Heat-treated (%)	Non-heat treated (%)
		2.85 ± 0.23	69.73 ± 0.45	8.62 ± 0.48	70.6 ± 0.56	5.92 ± 0.76	9.25 ± 0.54	12.6 ± 0.34	31 ± 0.54	2.1 ± 0.37	1.45 ± 0.53
	True density	3.68 ± 0.67		2.81 ± 0.16		13.86 ± 0.52		2.29 ± 0.34		14.68 ± 0.14	
Color	L*	93.39 ± 0.56		97.38 ± 0.28		83.11 ± 0.45		95.37 ± 0.67		89.7 ± 0.89	
	a*	0.47 ± 0.11		0.08 ± 0.04		0.11 ± 0.09		0.23 ± 0.16		0.01 ± 0.09	
	b*	8.24 ± 0.68		2.89 ± 0.33		2.75 ± 0.11		2.76 ± 0.87		1.99 ± 0.78	

[* microwave modified WCS (MD-WCS), microwave modified PS (MD-PS), autoclave freeze-dried WCS (AF-WCS), autoclave freeze-dried 20% PS (AF-20PS), autoclave freeze-dried 10% PS (AF-10PS)]

Calorific value

The calorific value is shown in Table 3 and the highest calorie content was found in MD-WCS and the lowest in AF-WCS. The calorific value of the samples viz., MD-WCS, MD-PS, AF-WCS, AF-20PS and AF-10PS was 357.58 kcal, 357.50 kcal, 341.17 kcal, 352.36 kcal and 345.65 kcal, respectively. The calorific value AF-WCS was the same with whole-wheat flour and MD-WCS possessed similar value with parboiled bulgar wheat. The calorific value of dried tapioca chips as noted by Gopalan et al. (2007) was 338 kcal/100 g which is in line with the present study. The modified cassava starch found higher calorific value as compared to dried tapioca chips (Gopalan et al. 2007). The above study can conclude that modified cassava starch is also calorie rich starch and one can choose it as ingredient for designing calorie dense food product.

FT-IR

Based on the findings of FT-IR spectra (Fig. 2), MD-DFS, MD-PS, MD-WCS, and AF-20PS exhibited the FT-IR spectra of 574 cm^{-1}, 1022 cm^{-1}, 1371 cm^{-1}, 1648 cm^{-1}, 2931 cm^{-1}, 3388 $cm^{-1}$and there were altogether six prominent peaks found between 4500–500 cm^{-1}. The prominent peak pattern of AF-10PS can be seen at around 1366 cm^{-1}, 1648 cm^{-1}, 2924 cm^{-1}, 4000 cm^{-1}. The spectra around 574 cm^{-1} indicated the skeletal model of pyranose ring (Flores-Morales et al. 2012). The peak at around 1022 cm^{-1} showed the characteristic amorphous region, C–O of C–O–C (Flores-Morales et al. 2012; Van Soest et al. 1994) and that of the peak around 1371 cm^{-1} denoted C–H symmetric bending of CH_3 (Flores-Morales et al. 2012; Van Soest et al. 1994). The peak at 1648 cm^{-1} is the behavior of –OH bending of adsorbed water (Abraham et al. 2011). The peak 2931 cm^{-1} is associated with the presence of the CH_2 stretching (Kaura´kova´ and Mathlouthi 1996). The presence of a broad wide peak at 3388 cm^{-1} denoted O–H stretching (Flores-Morales et al. 2012; Van Soest et al. 1994). The modified cassava starch-using microwave found similar FT-IR spectra however, the hydrothermal treated revealed different FT-IR spectra. The starch modification method affected the FT-IR spectra.

True density

The true density of all modified cassava starch is presented in Table 3. It was found in between 2.29 and 14.68. The treatment AF-10PS evinced the highest true density followed by AF-WCS and recorded the lowest in MD-PS, however, MD-PS and AF-20PS found almost similar true

Table 2 Color, nutritional information and hedonic sensory rating of cookies

Sample	Color			Nutritional information				Sensory analysis				
	L*	a*	b*	Energy (kcal)	Protein (g)	Carbohydrate (g)	Fat (g)	Dietary fiber (g)	Taste	Texture	Appearance	Aroma	Overall acceptability
TP1	51.34 ± 0.67	13.29 ± 0.65	35.26 ± 0.34	807.47 ± 21	11.30 ± 0.46	109.85 ± 0.69	33.62 ± 0.56	10.00 ± 0.34	3.2	3	3.6	3.6	3.2
TP2	53.33 ± 0.65	10.35 ± 0.37	33.28 ± 0.76	806.23 ± 0.46	9.31 ± 0.48	86.63 ± 0.21	33.63 ± 0.45	8.89 ± 0.43	3.2	3.2	3.6	3.2	5
TP3	59.07 ± 0.58	11.18 ± 0.92	33.54 ± 0.38	804.99 ± 0.39	9.31 ± 0.39	94.37 ± 0.54	33.27 ± 0.53	7.78 ± 0.56	3.2	2.4	4	4	4
TP4	61.99 ± 0.67	8.39 ± 0.67	30.85 ± 0.87	803.75 ± 0.76	8.31 ± 0.27	86.63 ± 0.72	33.09 ± 0.34	6.67 ± 0.41	3.8	4	4.4	5	8
TM1	42.04 ± 0.54	12.35 ± 0.76	33.83 ± 0.43	806.67 ± 0.48	11.22 ± 0.65	109.85 ± 0.76	33.63 ± 0.75	10.00 ± 0.65	3.12	4.4	5.2	5	7
TM2	50.43 ± 0.19	12.28 ± 0.97	34.66 ± 0.93	804.64 ± 0.38	10.14 ± 0.43	102.11 ± 0.64	33.45 ± 0.10	8.89 ± 0.56	4.4	5	5	3.8	6
TM3	48.13 ± 0.45	11.99 ± 0.47	33.71 ± 0.54	802.60 ± 0.58	9.06 ± 0.79	94.37 ± 0.76	33.27 ± 0.54	7.78 ± 0.64	6	6	4.4	4	5
TM4	58.16 ± 0.21	11.27 ± 0.36	36.24 ± 0.32	800.57 ± 0.58	7.98 ± 0.36	86.63 ± 0.54	33.09 ± 0.76	6.67 ± 0.74	3.6	3.8	3.8	4.4	5

Mean value of three replications with standard deviation

density. There was a drastic increase of true densities in autoclave treated cassava starch however, that finding was not true in case of AF-20PS. The above findings revealed that different physical modification of starch leads to different true density of modified starch.

Morphological properties

The SEM micrographs of modified starch are presented in Fig. 3. The starch modification method influenced the structures of starch in different ways. There was the absence of spherical structure in autoclave treatment modified starch while it was found in microwave-modified starch. AF-20PS showed flaky appearance while that of AF-10PS showed honeycombed structures. The changes in the autoclave treatment modified starch were possibly due to gelatinization, which caused swelling and damaged the native structure of starch granules. The process of size reduction by grinding may also be responsible for the damage of starch particles. The appearance of honeycomb and flaky appearance may be due to the difference in size reduction. MD-WCS, MD-PS, MD-DCS possess spherical smooth surfaces granules with the truncated end. The granular size of MD-WCS found within the range of 10.69–14.69 µm while that of MD-PS and MD-DCS revealed 8.96–17.47 µm and 8.53–12.93 µm, respectively. The above findings are in line with studies conducted by Ceballos et al. (2007). The granular size of 7–20 µm was found to be the most frequent granule size (Ceballos et al. 2007). The processing method greatly influenced the granule size of the cassava starch which can be seen in MD-WCS, MD-PS, MD-DCS, AF-10PS, and AF-20PS.

Color for modified starch

Color is one of the important criteria for the selection of cassava starch. The color value of modified cassava starch is presented in Table 3. L-scale indicates lightness vs. darkness, darkness ranged from 0–50 while that of lightness ranged from 51–100. Among all the modified starch L was found to be the highest in MD-PS and the lowest in AF-WCS. Redness vs. greenness is indicated by ‘a’ scale and it has both negative and positive values; a* positive value indicates redness while negative for greenness. All the samples had positive ‘a’ value, which means sample color, is more closed to red color. The ‘a’ value found highest in MD-WCS (0.47) and lowest in AF-10PS (0.01). Similarly, b scale indicates yellowness vs. blueness and has both positive and negative values. Yellowness is a positive value while blueness for negative value (CIE 2004). The ’b’ value of the sample had positive value in MD-WCS

Table 3 Nutritional information packaged foods of raw ingredients used for making cookies

Sl. No	Ingredients	Company		Nutritional information per 100 g				
				Energy (kcal)	Protein (g)	Carbohydrate (g)	Fat (g)	Dietary fibre (g)
a	Native cassava starch		PS	356.62	0.83			
b	Modified cassava starch		MD-PS	348.66				
1	Whole wheat flour	Aashirvaad	Whole wheat flour	369	10.8	77.4	1.8	11.1
2	Sugar powder (Baker's Caster Sugar)	Urban Platter Baker's Caster Sugar	Sugar powder	375	3.7	100	0	
3	Butter	Amul	Butter	722			80	
4	Baking powder	Rex	Baking powder	182	38.3	1.5	2.6	

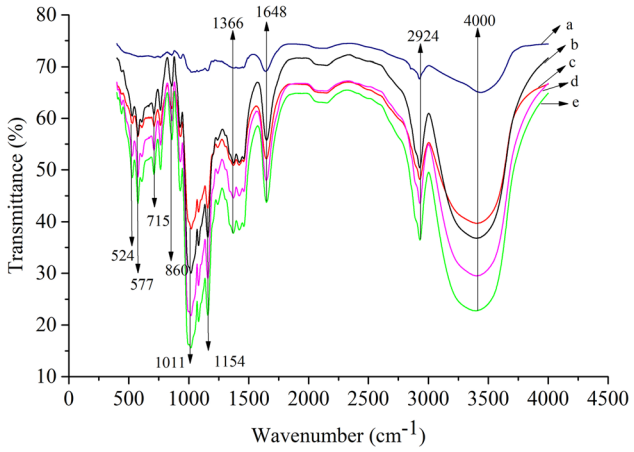

Fig.2 FTIR graph of modified cassava starches **a** autoclave freeze-dried 10% PS (AF-10PS), **b** autoclave freeze-dried 20% PS (AF-20PS), **c** microwave modified WCS (MD-WCS), **d** microwave modified PS (MD-PS), and **e** microwave modified DCS (MD-DCS)

having the highest value (8.24) and the lowest value in AF-10PS (1.99).

Digestion resistibility

The digestion resistibility (DS) test of native and modified cassava starches are presented in Table 3. The heat-treated starches were found lesser digestion resistibility as compared to non-heat treated starches. These findings were in line with the studies done by Yu et al. (2015). It was also reported that retrogradation had an effect on the digestibility and physicochemical properties of purple sweet potato flour and starch (Shu-Xi et al. 2015). The wide gap of DS between heat-treated and non-heat treated methods might be due to the gelatinization of starch in boiling water for 20 min. It made the gelatinized starch easily accessible by pancreatin enzyme thereby leading to decrease in resistibility of starch (Shu-Xi et al. 2015). The DS ranges of the heat-treated native and modified cassava starches were 2.1–59.64% and that of non-heat was 9.25–83.94%, respectively. In the non-heat treated method, the native cassava starch found 83.94%, which was higher than the modified starch. It was also reported that raw sweet potato starch DS was found 28.3 to 67.2% following a similar method (Zhang 2001). The DS percentage of non-heat treated microwaved starch found almost similar value in all the samples; however, it revealed a wider gap of DS percentage in case of heat-treated starch. It was observed that AF-20PS evinced a higher DS percentage as compared to AF-10PS. The thermal treatment found a direct effect on the DS of modified cassava starch.

Resistant starch of modified starch

The resistant starch (RS) of modified cassava starch is presented in Table 3. The higher amount of RS was observed in AF-10PS (10.51%) followed by AF-20PS (8.7%) and AF-WCS (8.14%), respectively. The variation of RS was observed in AF-10PS and AF-20PS, thus it can be concluded that the varying amount of water treatment in the sample can also influence the RSIII content. MD-WCS revealed the highest 61.62% resistant starch followed by MD-PS (57.17%). The microwave modified cassava starch was found to be greater resistant starch as compared to hydrothermally treated starch. RSIII is the retrograded starches, which are developed from unmodified starch or obtained after applications of food processing conditions (Ratnayake and Jackson 2008; Sanz et al. 2009). Autoclave treatment increased the RS and several workers have stated that wheat starch increased its RS from less than 1 to 9% after performing the autoclaved treatment (Siljestrm and

Asp 1985). The mechanism of starch modification included the hydrolysis of starch, which occurred during autoclaving, and consequently recrystallization happened during the incubation period. It was found that the raw cassava starch had a negligible amount of RSIII (0.44%). Onyango et al. (2006) reported that cassava starch autoclaved for 1 h at 121 °C and stored at the refrigerator for 24 h at 4 °C possessed 5.97% of RSIII. RS contents found higher when subjected to dry heat treatment as compared to wet-processed ones (Platel and Shurpalekar 1994). RSIII has shown high thermal stability and water-holding capacity than granular starch and it has been used as raw ingredients for various food applications (Haralampu 2000; Sanz et al. 2008).

Nutritional information

The nutritional content of the control and experimental cookies is presented in Table 2. The main source of protein in all the cookies is attributed to wheat flour. The protein, carbohydrate, and fibre found decreasing with the increase substitution level of flour by native and modified starch. These findings were also corroborated by Oluwamukomi et al. (2011), which reported that the increase in the cassava flour resulted in the decrease of protein content. The calorie content of control cookies followed a similar pattern like that of protein and vice-versa in the experimental cookies. One can consume three biscuits per serving which will give 150–152 cal, 1–2 g protein, 16–21 g carbohydrates, 6 g fat, and 1–2 g fiber. The experimental cookies TM1, TM2, TM3 and TM4 served beyond the nutritional benefits as the modified starch found to be rich in resistant starch which provides health benefits including the capacity to lower cholesterol and triglyceride level and increase absorption of vitamin and minerals (Raigond et al. 2015).

Color for cookies

The L* (darkness-lightness) of cookies ranged from 42–61. The L value of controlled cookies TP4 found to be 61.94 ± 0.67, which denoted the lightest color, while in the experimental cookies, TM4 shown a maximum L value of 58.16 ± 0.76 and minimum value 42.04 ± 0.54 in TM1 (Table 2). With the increase in substitution percentage of wheat flour by native starch, there was an increase in lightness (L*) of cookies and these values were in the order of TP3 > TP2 > TP1, respectively. In addition, a similar pattern was noticed in the cookies prepared using modified starch however, L value of TM2 was found to be greater than TM3. The cookies with modified starch were found to be darker in color as compared to native starch cookies. The a* (greenness- redness) value ranged from 8.39–13.29

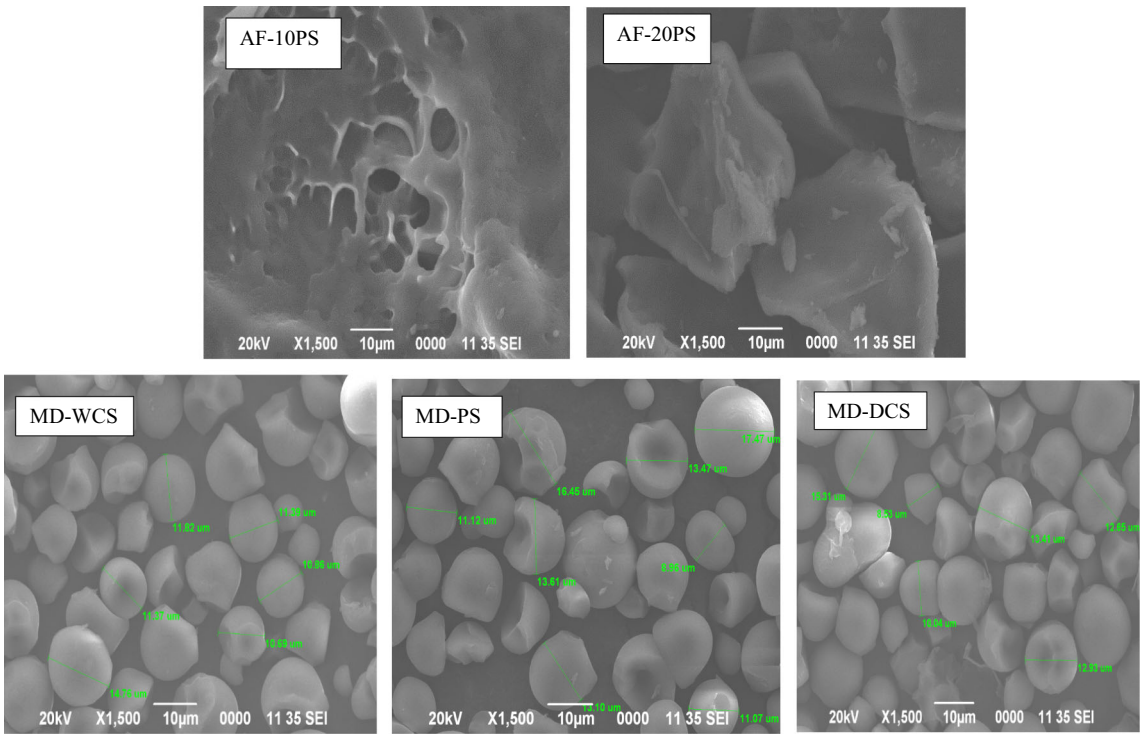

Fig.3 Scanning electron micrographs of modified cassava starches autoclave freeze-dried 10% PS (AF-10PS), autoclave freeze-dried 20% PS (AF-20PS), microwave modified WCS (MD-WCS), microwave modified PS (MD-PS), and microwave modified DCS (MD-DCS)

for the control sample. The maximum "a" value was found in TP1 and minimum value in TP4 while that of the experimental samples ranged from 11.27–12.35. The entire cookies samples shown positive value, which denoted the color closed to red. The b*-scale indicates yellowness vs. blueness, either it can possess positive or negative value (CIE Central Bureau; 2004). The highest b* value was found in TM4 followed by TP1 with a value of 36.24 and 35.26, respectively and the minimum "a" value was found in TP4 (30.85). The cookies exhibited more nearness to yellow color (CIE 2004). The results revealed that the level of wheat flour substitution has a direct effect on the color of the final cookies. The working efficiency of the baking oven also influenced the overall color quality of cookies.

Sensory analysis

The hedonic rating score by 25 panelists are shown in Table 2. The conventional wheat flour, which was used for the preparation of cookies could be substituted with the extracted starch either in the form of native and modified starch. The composite flour with 40% cassava starch (TP4) found to be the best cookies among all the samples based on the overall acceptability score. The studies on biscuit prepared from 40% cassava flour substitution revealed that the sensory attributes viz., color, aroma, and overall acceptability were acceptable (Oluwamukomi et al. 2011). All the cookies viz., TP1, TP2, TP3, TP4, TM1, TM2, TM3 and TM4 with native or modified starch possessed different attributes with the sensory score found within acceptable ranges (on and above score value 5). In case of texture, the control cookies were found to be harder. It might be attributed to the cementing effect caused by cassava starch and thereby causing hard texture. However, the experimental cookies texture was found to be soft. The overall quality attributes of cookies can be improved if the samples get uniform oven temperatures. The appearance of cookies found acceptable with favorable color and aroma. The cookies can further be optimized to get a better product with addition of ingredients like guar gum that can fill up the gluten lacking power caused by the level of wheat flour substitution. From the above analysis, one can observe that the texture of cookies was greatly influenced by cassava starch quality. The native starch led to hard cookies while modified starch led to soft cookies in terms of its texture.

Conclusion

The modified cassava starch is calorie rich starch and can be used as an ingredient for calorie dense functional foods with addition of RS. The change in starch granule structure was observed in hydrothermal treated modified starch leading to enzymatically susceptible starch. The thermal treatment affects starch digestion resistibility and a higher amount of resistant starch can be achieved using microwave treatment compared to hydrothermal treatment. The different starch derivatives can be obtained by using this modification technique depending on the need and possible potential applications. The development of cookies using modified starch MD-PS at the substitution level of 10–40% wheat flour can further be improved using cookies binding additives or ingredients. The quality attributes of cookies using modified starch at the substitution level of 40% were in the acceptability ranges. The developed modified starch will surely serve the purposes of providing functional ingredients with added health benefits beyond nutrition.

Acknowledgment The financial help received from the University Grants Commission (UGC), New Delhi in the form of NET-JRF (No. 1474/NET-DEC.2013) is duly acknowledged.

Author contributions Singamayum Khurshida carried out the experiments, wrote the manuscript with support from Sankar Chandra Deka (Supervisor), and prepared the samples. Ms. Khurshida conceived the original idea. Sankar Chandra Deka (Supervisor) helped in every technical aspect and monitored the research work and in the whole project he supervised wherever it was required.

Funding No research funding was received externally but the host institute Tezpur University, Assam helped in the work. The 1st Author got Fellowship for her PhD research work from UGC, New Delhi.

Compliance with ethical standards

Conflict of interest There is no conflict of interest or competing interests among the Authors.

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