

Tuning the Chemical and Thermo-Mechanical Properties of Cassava Starch Thin Films to Produce Biodegradable Packaging Materials

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Abstract

Starch is a renewable resource and starch films play a vital role as an alternative for synthetic polymers in packaging applications. However, the films prepared from native starch fail to meet the process or product requirements due to high water absorption and inferior mechanical properties. In order to avoid these drawbacks, and to enhance the desired properties, starch can be modified using acid hydrolysis. In this study, the effects of acid hydrolysis time on the structural, thermal, and chemical properties of cassava starch and cassava starch thin films were investigated. Native cassava starch was hydrolyzed using 2.2 M hydrochloric acid with varying time intervals. With the increase of hydrolysis time, the relative crystallinity of cassava starch increased while the thermal decomposition temperature decreased in cassava starch. XRD and ^{13}C -NMR spectrums results show that, cassava starch has been subjected to polymorphism changes from A (monoclinic cell) to B (hexagonal unit cell) due to the acid hydrolysis treatment. FTIR and TGA analysis showed that, the moisture absorbance of cassava starch decreased significantly as a result of the acid hydrolysis treatment. The acid hydrolyzed samples showed up to 31.79 % reduction of moisture content compared to the native starch samples. Also, the films prepared from acid hydrolyzed starch showed up to 25.12% reduction of water absorption compared to that prepared from native starch. Acid hydrolysis treatment significantly impacted the mechanical behavior of starch-based films. The tensile strength of cassava starch-based films improved continuously with acid hydrolysis time, reaching a maximum of 5.67 MPa. However, the ductility of the films was negatively impacted when the starch was subjected to acid hydrolysis. The films prepared using acid hydrolyzed starch showed a 12.78 % reduction of elongation compared to that prepared with native cassava starch, despite with minimum dependence of acid hydrolysis time.

Introduction

Starch is one of the most abundant polysaccharides found in plant storage organs such as seeds and swollen stems. Granules of starch are semi crystalline particles which contain two homopolymers known as amylose and amylopectin. Starch granule size, morphology, composition, and supramolecular structure are highly dependent on the plant source (Parker and Ring, 2001; Bertolini, 2010). Some of the main starch sources are corn, cassava, wheat, and potato. Components of cassava starch depend on the geographical locations, variety, and the age of the particular plants (Morgan and Choct, 2016). Cassava starch typically contains 17 % of amylose and 83 % of amylopectin (Morgan and Choct, 2016). The physicochemical properties of starch depend on the ratio among amylose and amylopectin (Corcuera et al., 2007 ; Sasaki et al., 2000; Duan et al., 2012). When compared with amylose, usually, amylopectin is a highly branched molecule and larger than amylose in size (Tang et al., 2006).

Starch plays a significant role as a raw material for the production of bioplastic, paper, textile, and in the food industries (Whistler et al., 2012). Hence, it is an excellent opportunity to add value to cassava which is grown in the tropical environment without any fertilizer (Wahyuningtiyas and Suryanto, 2017). Despite the fact that, native starch is used because of its thickening and gelling capacities, for a number of applications, properties of native starches fail to meet process or product requirements (Waterschoot et al., 2014). It is a well-known fact that, native cassava starch is not suitable for industrial applications due to its poor mechanical and thermal properties. Therefore, in order to avoid these natural limitations of native starch, starch modification is of high importance. Among widely used starch modification techniques, physical methods (moisture, heat, high pressure, and radiation), chemical methods (acid hydrolysis, cross-linking, esterification, etherification, etc.) and enzymatic methods play an important role (Chen et al., 2018; Shrestha and Halley, 2014 ; Bemiller, 2018). Acid hydrolysis is performed using either sulfuric acid or hydrochloric acid (Gerard et al., 2002). The acid modification changes the physical and chemical properties of starch in an effective way (Bemiller, 2018).

Vermeylet et al., (2004) reported that acid hydrolysis has caused the changes of polymorphic transitions in the tapioca starch and these changes depend on the particular source of starch and the degree of acid hydrolysis. The findings of Sakkara et al., (2019) indicate a reduction of hydrophilicity and moisture content of maize starch films prepared under acidic pH. Zhang et al., (2019) have prepared the acid hydrolyzed pea starch and increase of tensile strength and reduction of

water vapor permeability have been observed. Most of the previous studies on acid hydrolysis of starch were focused on the physiochemical changes with the acid hydrolysis temperature, stirring time, and acid concentration. However, none of these studies have investigated the impact of acid hydrolysis on both thermo-mechanical properties and water absorption of cassava starch based thin films. Therefore, in this study, cassava starch was modified using hydrochloric acid (2.2 M) at different stirring times (30, 60 and 90 mins). The changes of structural, thermal and mechanical properties of the films were investigated. The aim of this research was mainly focused on discovering appropriate acid hydrolysis conditions to prepare cassava starch-based films with improved water resistance and thermo-mechanical properties.

Experimental

Materials

Conc. HCl and NaOH were purchased from Sigma Aldrich Co. (St. Louis, MO). All the reagents used were of analytical reagent grade and used without further purification. Amylose and Amylopectin were purchased from Sigma Aldrich (Merck Group, Germany).

Extraction of the cassava starch

Cassava starch was extracted in the laboratory according to the wet method described by Benesi et al., (2004). The extracted - dried cassava starch was passed through a 100-mesh sieve before using for further experiments. Moisture, protein, fat, ash, and the crude fiber content of the cassava starch were determined using Association of Official Analytical Chemists (AOAC) 920.36, 984.13, 948.22, 923.03 (2000), and AOAC 962.09(2005) standards, respectively. All the analyses were carried out in triplicate.

Table 1
Composition of the extracted cassava starch

Components	Percentage (%)
Moisture	12 ± (0.01)
Protein	0.66 ± (0.00)
Fat	0.19 ± (0.00)
Ash	0.23 ± (0.00)
Crude fiber	0.10 ± (0.01)
The percentage data depicted in Table 1 are the means of triplicates.	

Acid hydrolysis

In order to obtain acid hydrolyzed cassava starch, the method described by Chung et al., (2003) was used while employed with some modifications. Initially, 5.00 g of cassava starch was mixed with 50.0 ml of (2.2 M) HCl. Next, solutions were stirred at 200 rpm at 45 °C for 30, 60, and 90 min. Then, acid-treated starch slurry was neutralized using 1 M sodium hydroxide solution. After that, the acid-modified cassava starch was washed with distilled water. Subsequently, samples were freeze-dried until a powder was obtained. Each trial was triplicated.

The native and modified starch samples were named during the experiments as follows.

CS - Native cassava starch

AH 0.5 - Acid hydrolyzed cassava starch treated for 30 min

AH 1.0 - Acid hydrolyzed cassava starch treated for 60 min

AH 1.5 - Acid hydrolyzed cassava starch treated for 90 min

Characterization:

X-ray diffraction (XRD)

The X-ray diffraction patterns were obtained for native cassava starch and acid hydrolyzed cassava starch, using a diffractometer (Rigaku Ultima IV) with the Scintillation counter detector at 40 kV and 30 mA with K- α filter. The XRD spectra were recorded over an angular range (2θ) of 2 to 45° and the scan rate was maintained at 2°/min. The relative crystallinity (RC) of scattering spectra was calculated as the ratio of the sharp peaks (crystalline peaks) to the total peaks (Both crystalline and Amorphous line) shown in Eq. 1 according to the method described by the (Utrilla-coello et al., 2014).

$$RC (\%) = \frac{A_c}{A_t} \dots\dots\dots (1)$$

Where A_c is the Value of the area under the curve corresponding to the crystalline portion and A_t is the total area of the diffractograms

Solid-state Carbon-13 nuclear magnetic resonance (¹³C-NMR)

The ¹³C CP-MAS solid-state NMR spectra were obtained by using a Bruker Avance III 400 NMR spectrometer. The samples were spun at a rate of 5 kHz in a 4 mm zirconia rotor. The ¹³C CP-MAS NMR spectra were recorded using a Total Suppression of Spinning Sidebands (TOSS), pulse sequence. The chemical shifts were externally referenced to 176.03 ppm for the carbonyl carbon of glycine.

Starch Granules Morphology

Native cassava starch and modified starch granules morphology were studied using Scanning Electron Microscope (SEM) (ZEISS, Germany). The morphologies were evaluated at 2500× magnification and samples were coated with gold, and then examined at an acceleration potential of 10 kV.

Thermogravimetric Analysis (TGA)

Thermal degradation and moisture content of all the samples were evaluated using the TGA 5500 (TA instruments, USA) under the nitrogen atmosphere. 100 μ l platinum crucibles were used with a heating rate of 10 °C /min while maintaining the temperature range from 25 °C to 650 °C (Stawski, 2008). Thermal degradation temperature and the moisture content were calculated using the TRIOS software.

Fourier Transforms Infrared spectroscopy (FTIR)

Characteristic peaks for the cassava starch and modified cassava starch were obtained using FTIR Spectrum two (PerkinElmer, USA) equipped with ATR reflectance cell. Spectra were observed in the ranging 500–4000 cm^{-1} . For each sample, 4 scans were taken at a resolution of 4 cm^{-1} . FTIR spectra were analyzed using the Origin software.

Preparation of Cassava starch based thin films

Thin films were prepared by using the method adapted by Belibi et al., (2014). Initially, native and acid hydrolyzed cassava starch (5 % (w/w) total film solution) was dispersed separately in distilled water with the corresponding content of glycerol (30 wt.% on the dry starch basis) at room temperature and stirred for 10 minutes on a magnetic stirrer. After that, mixtures were stirred at 80 °C for 45 minutes. Then the films were obtained by casting the hot suspension into petri dishes. These dishes were left at room temperature for 6 hours to allow bubbles to dissipate. Then, the samples were dried in an oven with air circulation at 65°C for five hours. The dishes were kept in a desiccator and finally, the dry films were removed from the dishes.

Mechanical Test

Mechanical property measurements (Tensile strength, and Percentage Elongation at break) were obtained according to ASTM D 882–02. The tensile strength test was performed using the Intron 3365 Universal Testing machine (Instron Ltd, Buckinghamshire). The crosshead speed was fixed as 25 mm/min. The samples were prepared according to the dimensions provided by the standard. Specimens were cut from the film samples (five different specimens) and each sample had a width of 30 mm and a length of 110 mm. For each test, five samples were analyzed. During the stretching, tensile strength (MPa) and Elongation at break were recorded. The mechanical properties were as the average value calculated from the attained results.

Biodegradability test

The biodegradability test was carried out according to the aerobic compost environment test. The acid hydrolyzed cassava starch thin films were cut into pieces of 2.0 x 2.0 cm. The compost soil consists of 14.07 % of total C and 1.10% of total N, respectively. The samples were buried inside the soil at a depth of 3 cm at 25 °C and water was sprayed to maintain the moisture of the compost. The weight of the samples was measured after 15 days according to the given Eq. (2):

$$\text{Weight Loss (\%)} = \frac{W_1 - W_0}{W_0} \times 100 \dots\dots\dots (2)$$

Where W_0 and W_1 are the weights of thin films before and after the test, respectively. The reported results represent the average of three replicates in each sample.

Water Absorption of the films

The water absorption of the cassava starch films was measured according to ASTM D570-98. Initially, all the samples were conditioned at 50 °C for 24 hours and weighed (M_0) before being tested. Next, the samples were immersed in distilled water. After 2 hours, all the specimens were removed from water, dried with a cloth, and immediately weighed (M_1). The water absorption data of the films were obtained by soaking them in water for 2 hours. After that, those samples were soaked in water for another 24 hours and weighed (M_2). The water absorption capacities of the thin films were calculated as follows.

$$\text{Water absorption (\%) at 2 hrs} = \frac{M_1 - M_0}{M_0} \times 100 \dots\dots\dots (3)$$

$$\text{Water absorption (\%) at 24 hrs} = \frac{M_2 - M_0}{M_0} \times 100 \dots\dots\dots (4)$$

Results And Discussion

X-ray diffraction (XRD)

Starch is a semi-crystalline natural polymeric material where it has both amorphous and crystalline regions. The amorphous regions of starch granules mainly consist of amylose and some branches of amylopectin, while the crystalline areas are made out of amylopectin (Bertolini, 2010). The relative crystallinity of starch depends on the environmental conditions of the cultivation which determines the ratio between amylose and amylopectin (Stawski,2008). Lemos et al., (2018) and Beninca et al., (2013) have reported that the relative crystallinity of cassava starch as 17.5 % and 22.65%, respectively. However, the relative crystallinity of Sri Lankan cassava starch has not been reported yet. In this study, the relative crystallinity of Sri Lankan cassava starch determined by XRD was 23.87%.

Table 2
Relative crystallinity and peak positions of the native and acid hydrolyzed cassava starch samples.

Sample	Relative Crystallinity (%)	Peaks ($2\theta^\circ$)
CS	23.87	15.01, 17.03, 18.04, 20.06, 23.19
AH 0.5	31.1	14.81, 16.83, 17.82, 20.06, 22.78, 31.66
AH 1.0	33.1	14.93, 16.84, 17.73, 19.75, 22.65, 31.72
AH 1.5	33.3	14.84, 16.74, 17.75, 19.76, 22.56, 31.70

XRD spectrum of native (CS) and acid hydrolyzed (AH) cassava starch samples at different hydrolysis time periods was shown in Fig. 1. Calculated relative crystallinity and peak positions of the native and acid hydrolyzed cassava starch samples are shown in Table 2. First four prominent peaks ($2\theta = 15, 17, 18, 20$ and 23°) indicate the A type crystallinity of cassava starch (Utrilla-coello et al., 2014). Note that these four peaks are visible for both native and acid hydrolyzed cassava starch samples. As indicated in Fig. 1 and Table 2, cassava starch granules subjected to acid hydrolysis increases the relative crystallinity along with the hydrolysis time. Similar results were reported by Zhang et al., (2019) where the relative crystallinity increased in pea starch with the hydrolyzed time. The crystalline lamella is more resistance to chemical reactions than the amorphous region and this phenomenon reflects the crystallinity data shown in Table 2. According to XRD data, the highest crystallinity (33.3 %) was observed for the acid hydrolyzed cassava starch sample hydrolyzed for 90 mins.

Usually, acid hydrolysis causes the change of crystalline polymorphs of both A and B type starch (Wang et al., 2015). These acid hydrolyzed cassava starch samples show B-crystallites compared to that of their native cassava starch peaks according to the data depicted in Table 2. Therefore, it is conclusive that, acid hydrolysis could improve not only total crystallinity of cassava starch, but also the crystallinity level of B-crystallites. This improvement in crystallinity is demonstrated by the increased peak intensity at $\sim 31^\circ$ (2θ) as depicted in Fig. 1. Moreover, Garcia et al., (1996) and Vermeylen et al., (2004) have reported the change of polymorphs of cassava starch from A to B, and it has been well matched with the present work-study. Two hypotheses have been proposed in order to describe this change of polymorphism in this study. The first one is, some A-type crystallites could be metastable, and the removal of a part of A-type crystallites may cause the reorganization of remaining chains into more stable crystalline B-type (Fig. 2). The second one is based on the assumption that, there might be some B-type polymorphs in native cassava starch that are too small to be detected by XRD (Wang et al., 2015).

Figure 2 shows the mechanism for acid hydrolysis of cassava starch granules. As demonstrated in Fig. 2(d), acid hydrolysis breakdown the amylose molecules and it induces the formation of small helix of amylose, D- glucose monomers, and liner amylose chains. The acid hydrolysis cleaves the covalent linkages (1–6, glycosidic bonds) between the double helices of the amylopectin in the amorphous region (Wang et al., 2015). Afterwards, rearrangement of amylopectin double helices in the lateral or axial translation and filling up of crystallite cavities with water molecules cause the polymorphous changes of cassava starch (Shown in Fig. 2 (e) and (f)).

Carbon-13 Nuclear Magnetic Resonance ($^{13}\text{C-NMR}$)

Molecular order in starch granules can be determined by using both X-ray diffraction and ^{13}C solid-state NMR (Gidley, 2014). However, by using XRD, it is not able to detect either the double helices or whether they are packed in the short-range distance or not. ^{13}C solid-state NMR is mostly used to analyze the molecular structure of starch granules at the single chain (amorphous) and double helix (ordered) (Gidley and Bociek, 1985).

^{13}C solid-state NMR of C-1 resonance gives information about the crystalline and the non-crystalline nature of the starch chains. Although the information about the structure type of the starch granules is given by the multiplicity (Triplet or

doublet) of the C-1 resonance, the ^{13}C -NMR resonance for C-1 (90–110 ppm) is related to the crystalline structure of starch granules. A-type starch shows a triplet at C-1 resonance (The two-fold axis generates the double helix and the C-1 peak in A-type starch spectra is a triplet). B-type starch shows a doublet at C-1 resonance. Although for C-type starch, C-1 resonances mainly depend on the relative proportion of A- and B-type polymorphs (Atichokudomchai et al., 2004), Fig. 3 shows that the native cassava starch consists only of A-type starch (hexagonal arrangement of the double helices) (Gidley, 2014). Several significant changes have occurred in the molecular structure of starch granules during acid hydrolysis. It can be monitored by using ^{13}C -NMR spectra (Fig. 3). In the C-1 region of the spectrum, (90–110 ppm) it shows the doublet which indicates the changing of crystalline structure into B type with the variation of acid hydrolysis time. The signal at 81–82 ppm (C-4) indicates the amorphous regions of cassava starch. Changes in the ^{13}C -NMR spectra also occur in the C-2, C-3, C-4 and C-5 regions (68–78 ppm), where the signals have become increasingly sharper. The same observation was also reported by Atichokudomchai et al., (2001) for tapioca starch.

Starch Granules Morphology

The average diameter of the native cassava starch granules obtained from SEM ranged from 12 to 20 μm and regular oval- or sphere-like shapes with smooth surfaces (Fig. 4). AH 0.5, AH 1.0 and AH 1.5 (see Fig. 4, b, c and d) and b) samples exhibited surface erosion on the surfaces of the starch granules. Note that the smaller sizes cassava granules showed the fragmentation and deformation due to the acid hydrolysis. According to the Fig. 4 with the increased acid hydrolysis time, the surface erosion and fragmentation increased. As previously mentioned, it is caused by the attack of acid to the amorphous regions. It is suggested that, the amorphous regions on the periphery of the granule were preferentially attacked by acid during the acid hydrolysis treatment process.

Thermogravimetric Analysis (TGA)

Table 3
Moisture and Thermal Decomposition Temperature of the native and acid-modified cassava starch at a different stirring time periods

	Moisture content / (%)	Thermal Decomposition Temperature / ($^{\circ}\text{C}$)	Mass Loss / (%)
CS	9.28	330.79	67.385
AH 0.5	6.33	309.74	41.15
AH 1.0	5.949	307.91	35.435
AH 1.5	5.540	305.34	30.928

The thermogravimetric (TG) and corresponding differential thermogravimetric (DTG) profiles of native and acid hydrolyzed cassava starch samples are shown in Figure 5. The TGA profiles (see event a) of the samples show two distinct weight loss regions in the temperature range of 30-100 $^{\circ}\text{C}$ and 250-450 $^{\circ}\text{C}$. The transition (a) (30-100 $^{\circ}\text{C}$) is due to the evaporation of physically adsorbed water in starch samples. The increase of acid hydrolysis time reduces the moisture content, decomposition temperature, and mass loss at decomposition temperature. Therefore, the decrease of moisture content shows a reduction of amorphous regions of the starch granules. This observation can also be supported by the XRD data which performs an increase in relative crystallinity.

The second thermal event (see event b) can be seen in the temperature range of 250–450 $^{\circ}\text{C}$ for both native and acid hydrolyzed cassava starch. The decomposition temperature and the weight loss of all the acid hydrolyzed samples (see Table 3) decreased with increase of acid hydrolysis time due to the reduction of thermal stability of cassava starch during acid hydrolysis. Thermal stability mainly depends on the crystallinity and the amylopectin content of the starch (Miao et al., 2011). Liu et al., (2009) has also reported a decrease in the decomposition temperature with the decrease of amylose

content. According to our results, we also believe that, the reduction of amylose content by the acid hydrolysis could be the main reason for the decrease of both decomposition temperature and weight loss.

Fourier Transforms Infrared spectroscopy (FTIR)

FTIR spectrums of acid hydrolyzed starch were compared with the native cassava starch as shown in Fig. 6. According to Fig. 6, all samples show the O-H stretching bands for aliphatic compounds occur in the range of 3250 cm^{-1} (Almeida and Alves, 2010; Zhang et al., 2013). The band at 2937 cm^{-1} is attributed to the symmetrical and asymmetrical C-H stretching. The band at 1637 cm^{-1} indicates the flexion of the O-H of the water which indicates that, starch is hygroscopic. The amplitude of the band indicates the presence of intermolecular hydrogen bonds. FTIR spectrum shows that, with the increment of acid hydrolyzed time, the amplitude of the 1637 cm^{-1} band decreased. It implies that the absorbance of H_2O decreased as discussed in TGA. Therefore, based on the above facts, it is conclusive that, acid hydrolysis causes a decrease in water absorption. The peaks obtained at 1417 and 1341 cm^{-1} are the C-H bending vibrations which is a characteristic of the polysaccharides and can be attributed to the strain deformations of C-O-C. The band at $1100\text{--}1152\text{ cm}^{-1}$ is for C-O, C-C, and C-O-H stretching. The band at $1100\text{--}900\text{ cm}^{-1}$ corresponds to the C-O-H bending vibrations (Lemos et al., 2018).

Mechanical Test

The mechanical properties of acid hydrolyzed and native cassava starch films are shown in Fig. 7. With the increment of hydrolysis time, the Tensile Strength (TS) has increased significantly ($p < 0.05$). However, the completely opposite trend was observed for the elongation at break (E%). These findings support the increase of crystallinity of cassava starch by acid hydrolysis. When crystallinity increases, it reduces the amorphous area, which increases the tensile strength and limits the elongation at break. This confirms the previous findings in the literature reported by Zhang et al., (2019) and Cheng et al., (2007). Although results indicate the increase of tensile strength along with the hydrolysis time, there is no significant increase of the tensile strength when the hydrolysis time was increased from 60 to 90 mins. This can be described to the beginning of breaking down of the both amylose and disordered amylopectin. Based on the tensile strength results obtained, 60 mins acid hydrolyzation time can be considered as the effective time to prepare films.

Biodegradability test

The biodegradation rate with the hydrolysis time is shown in Fig. 8. In soil, water diffuses into the cassava starch chain causing swelling and enhancing biodegradation due to increases in microbial growths. Then microorganisms attack and consume the cassava starch leading to a fracture of the film structure. Also, the burial environment parameters (temperature, pH, moisture, nutrition) have a great impact on the biodegradation of films (Seligra et al., 2016). According to the data in Fig. 8, cassava starch thin films have highest biodegradation rate and 30 min acid hydrolyzed thin film has the lowest one. The reason is due to the reduction of the amorphous region as explained previously.

Water absorption

Starch is sensitive to water and this behavior limits their industrial applications. However, water absorption of starch materials is of high importance to promote their biodegradability. The bio-based materials must be hydrophobic for industrial applications but they must absorb water after using, to promote degradability since; most microorganisms are efficient in high moisture environments (Nguyen et al., 2016). There was a significant positive correlation between acid hydrolysis time and water absorption. The water absorption of films is demonstrated in Fig. 9. Native cassava thin films have high water uptake rates at 2 hrs. and 24 hrs. immersed time periods. The most remarkable result to emerge from the data is that, the acid hydrolysis has created a positive impact on the reduction of water absorption. The reason is due to the reduction of the amylose amount in starch. It leads to a lot of industrial applications such as biodegradable film preparation for packaging materials.

Comparison with other studies

Table 4

Comparison of the present study with previous acid hydrolyzed experiment data (TS; Tensile strength and WA; Water absorption at 2 hrs.)

Starch Type	Conditions	Relative Crystallinity (%)		TS (MPa)		WA (%) at 2 hrs.		Ref.
		Native	Max.	Native	Max.	Native	Min.	
Tapioca Starch	4 % of starch was stirred using conc. HCl stirred at room temperature Time- 12,24,48,96,192,384 and 768 hrs.	39.53	57.75 (768hrs.)	-	-	-	-	(Atichokudomchai et al.,2001)
Konjac Glucomannan (KGM)	35 g of starch was hydrolyzed using conc. HCl Room Temp. for 2 hrs. Volume- 10,20,30,50 and 70 ml	-	-	-	0.7 (30ml)	-	-	(Cheng et al., 2007)
Waxy Maize Starch	2.2 M HCl at 35°C Time- 3,8, and 15 days	26.47	39.17 (15 days)	-	-	-	-	(Miao et al., 2011)
Native Corn starch	15 g of starch was stirred using 3.16 M H ₂ SO ₄ (100 ml) at 35°C Time-0-15 days	-	42 (3 days)	-	-	-	-	(Utrilla-Coello et al., 2014)
Pea starch	10 g starch with 2.2.M HCl (100ml) at 36°C Time- 1,2,6,12,20 and 35 days	48	69 (20 days)	-	-	-	-	(Wang et al., 2012)
Pea starch	172.46 g of starch with 350 ml of 2% HCl at 45°C Time- 0.5,1.0, 1.5 and 2.0 hrs. The thin film was prepared using 4%of starch and 40% of Sorbitol	40	43.6 (2.5hr)	16	21 (2 hrs.)	-	-	(Zhang, et al., 2019)

Starch Type	Conditions	Relative Crystallinity (%)		TS (MPa)		WA (%) at 2 hrs.		Ref.
		Native	Max.	Native	Max.	Native	Min.	
Cassava Starch (Present Study)	5 g was hydrolyzed using 50 ml of 2.2 M HCl at 45°C Time- 30,60 and 90 mins The thin film was prepared using 5% of starch and glycerol (30 wt.% on the dry starch basis)	23.87	33.3 (90 mins)	5.04	5.67 (60 mins)	74.03	41.5 (30 mins)	

Table 4 compared the maximum relative crystallinity, tensile strength, and minimum water absorption of different acid hydrolyzed starch reported in literature with the present study. Based on the data depicted in Table 4, it's conclusive that, acid hydrolyzed cassava starch samples show good crystallinity and water absorption at the present condition(s).

Conclusions

This study has investigated the effect of acid hydrolysis treatment on the structural, thermal, and mechanical properties of thin films. The relative crystallinity of native cassava starch increased and gelatinization peak temperature is decreased with the acid hydrolysis time due to the reduction of the amylopectin molecules during the treatments. The acid hydrolyzed technique shows clear advantages through the reduction of the decomposition temperature and moisture absorbance in cassava starch. The structural polymorphous changes have occurred with acid hydrolyzing treatment and with the increase of relative crystallinity. Along with the acid hydrolysis, tensile strength is increased and elongation at break decreased. The present findings have important implications for solving water absorption of the cassava starch thin films due to the reduction of the amylopectin available in the cassava starch. It is conclusive that, acid hydrolysis can be used as an effective way to increase the tensile strength and to reduce the water absorption of the thin films. The amylose and amylopectin content of the acid-treated cassava starch should be further investigated to determine the amylose and amylopectin ratio of cassava starch.

Declarations

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Conflict of interest

The authors declare no conflict of interest, and the manuscript is approved by all authors. We confirm that neither the manuscript nor any parts of its content are currently under consideration or published in another journal.

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Figures

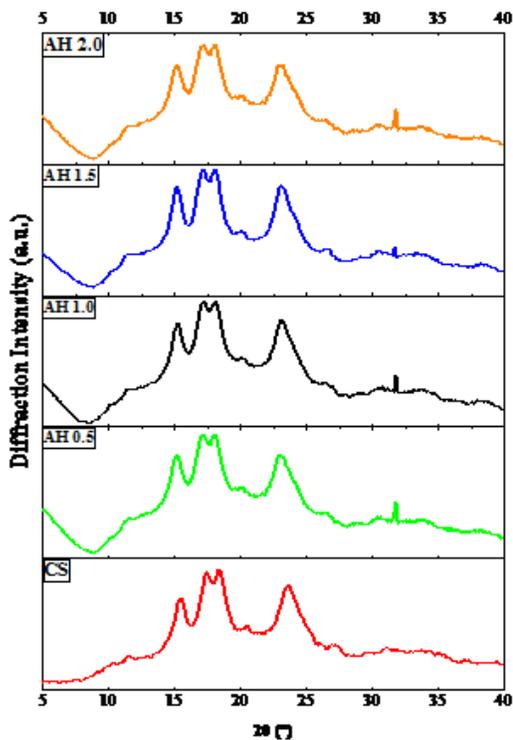


Figure 1

XRD diffractograms of native (CS) and acid hydrolyzed (AH) cassava starch samples at different hydrolysis time periods (AH 0.5, AH 1.0 and AH 1.5 AH are the 30, 60 and 90 mins stirring time of cassava starch at 45 oC, respectively).

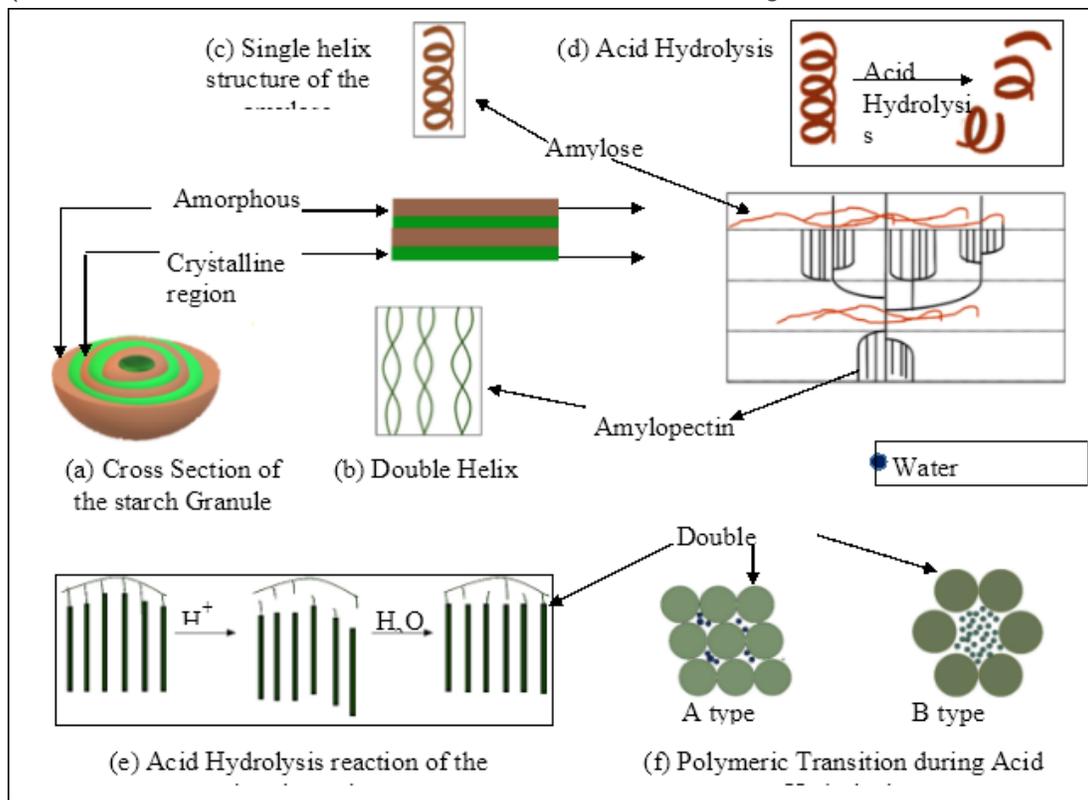


Figure 2

Mechanism for acid hydrolysis of cassava starch granules

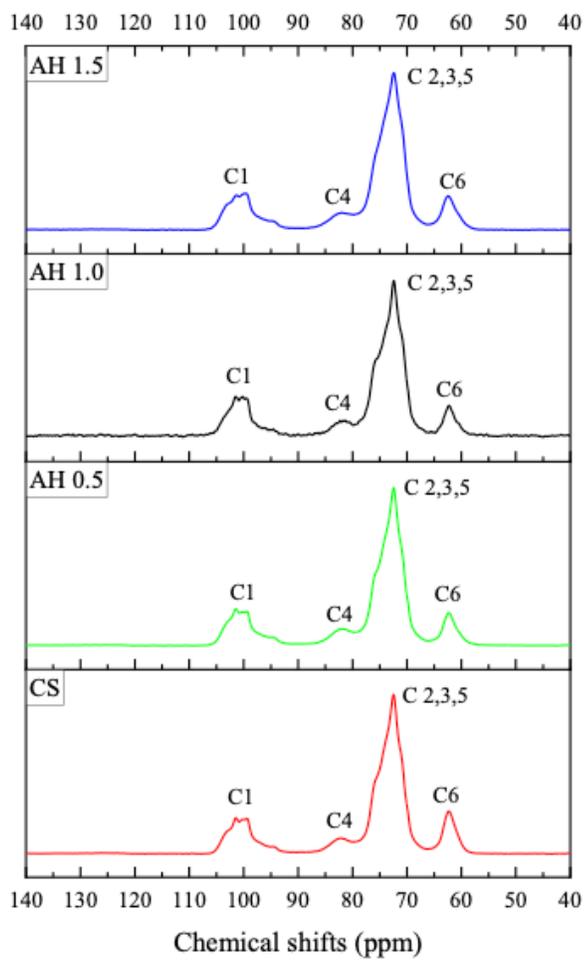


Figure 3

^{13}C CP/MAS NMR spectra of native and acid hydrolyzed cassava starch at different hydrolysis time periods (AH 0.5, AH 1.0 and AH 1.5 are the 30, 60 and 90 mins stirred cassava starch at 45 oC, respectively) and Repeating unit of the starch

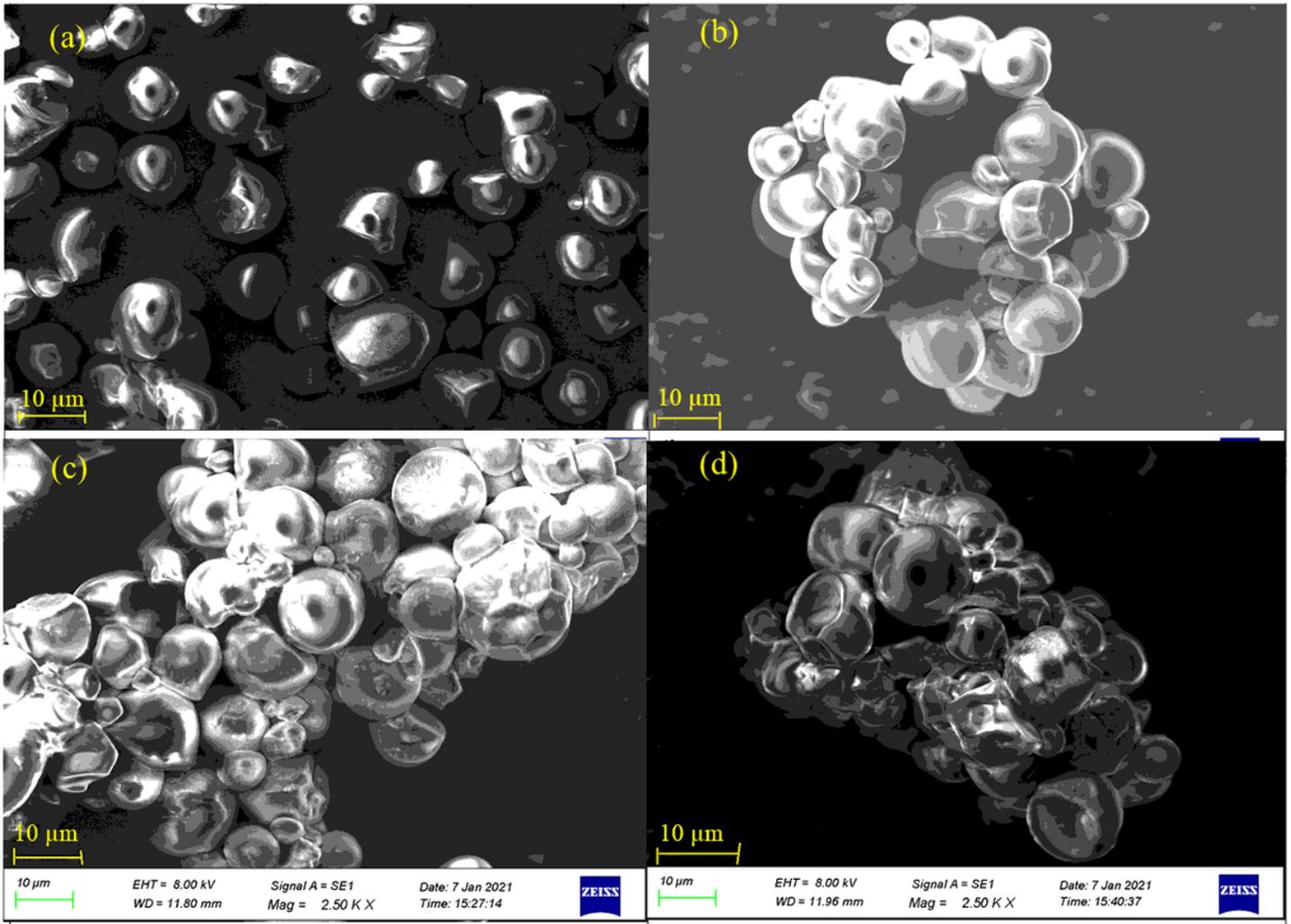


Figure 4

Scanning electron micrographs of native and acid-treated cassava starch granules. (a- native cassava starch and b, c, d - 30, 60 and 90 mins stirred cassava starch at 45 oC, respectively)

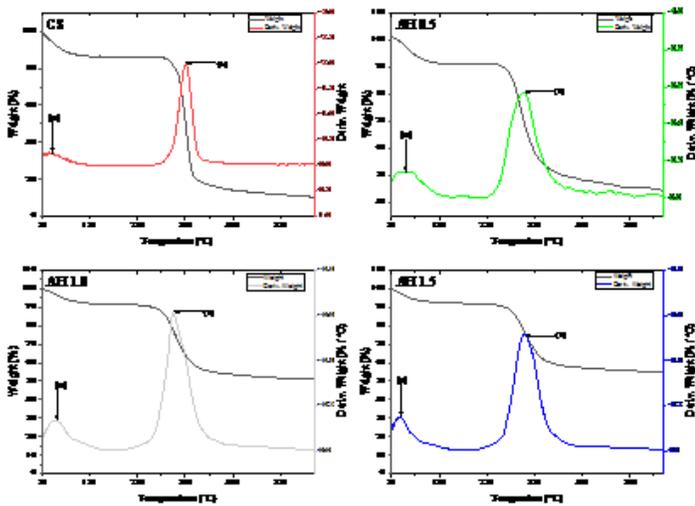


Figure 5

TGA/DTG curves for the native (CS) and acid hydrolyzed cassava starch (AH 0.5, AH 1.0 and AH 1.5 are the 30, 60 and 90 mins stirred cassava starch at 45 oC, respectively).

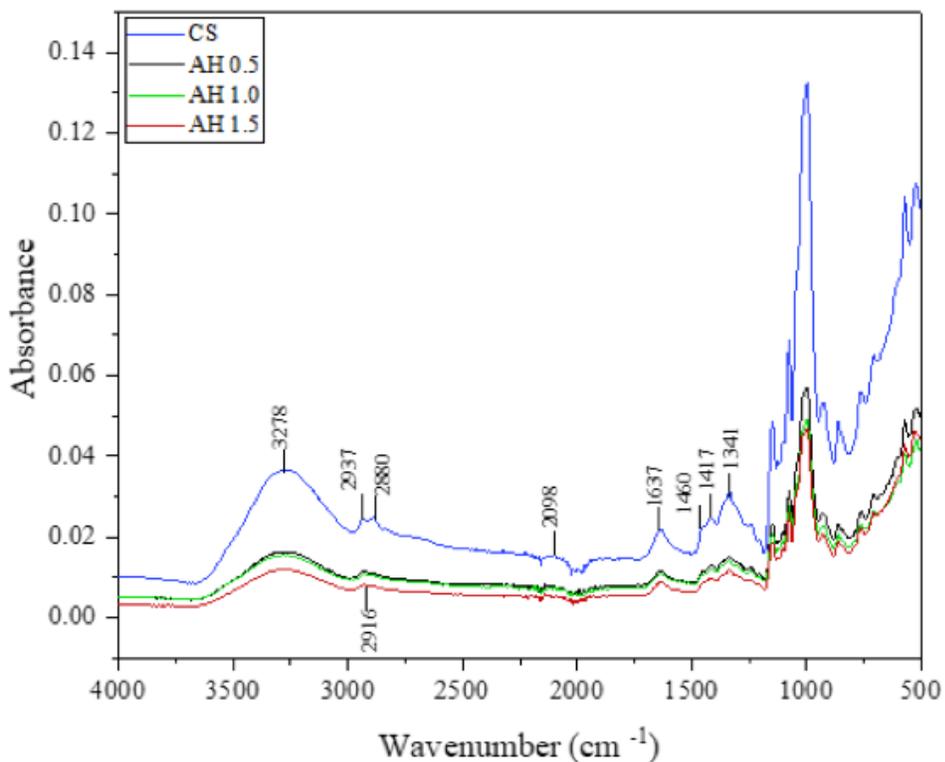


Figure 6

FTIR-ATR spectrum of the native and acid hydrolyzed cassava starch at different hydrolysis time periods (AH 0.5, AH 1.0 and AH 1.5 are the 30,60 and 90 mins stirred cassava starch at 45 oC, respectively).

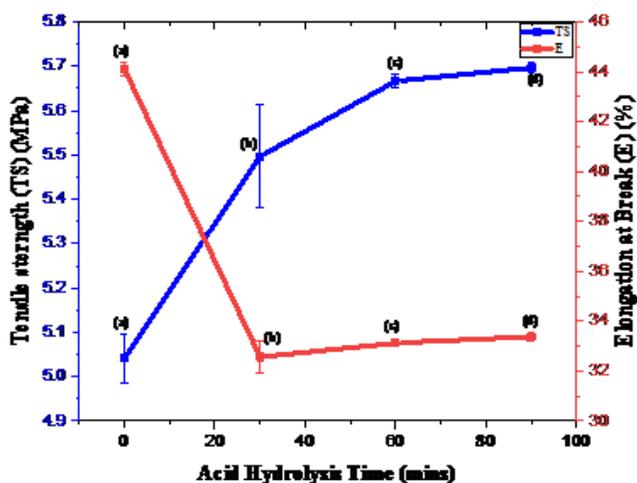


Figure 7

Tensile strength and elongation at break of native and acid hydrolyzed cassava starch thin films. (Data were means of five determinations \pm standard deviation. a- Cassava starch thin films, b, c, d are 30, 60 and 90 mins acid hydrolyzed cassava

starch thin films respectively).

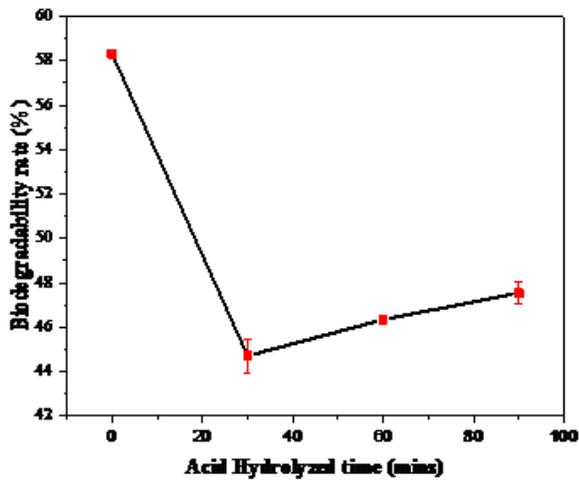


Figure 8

Biodegradability rate (%) of native and acid hydrolyzed cassava starch thin films. (Data were means of five determinations \pm standard deviation. 0 mins- Cassava starch thin films)

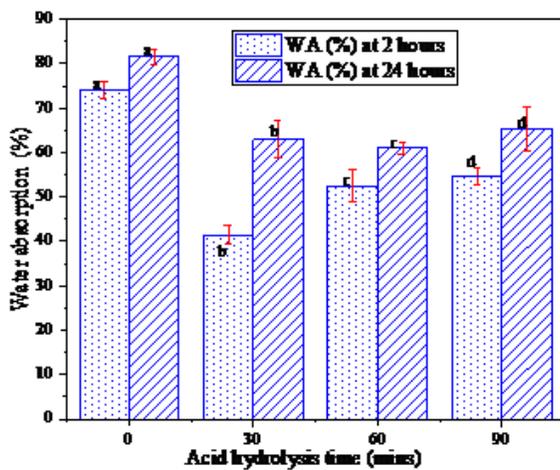


Figure 9

Water Absorption (WA) (%) of native and acid hydrolyzed cassava starch thin films. (Data were means of five determinations \pm standard deviation. a- Cassava starch thin films, b, c and d are 30, 60 and 90 mins acid hydrolyzed cassava starch thin films respectively).

Supplementary Files

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