A Comparative Study of the Structures, Crystallinities, Miller Indices, Crystal Parameters, and Particle Sizes of Microwave- and Saline Water-Treated Cassava Starch

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The structures, crystallinities, Miller indices, and particle sizes of cassava treated with microwave radiation or saline water were analysed and compared. Cassava was milled to sizes of 100 to 120 mesh and then dried under solar radiation for several days. The first set of substrates was treated by microwave radiation at 300 W for 10, 20, or 30 min or at 1000 W for 8 min. The second set of substrates was immersed in saline water for 5 days at salt concentrations of 3.43% or 10% (w/w). The treated substrates were characterised by x-ray diffraction, Fourier transform infra-red spectroscopy, and scanning electron microscopy, and the results were compared with the characteristics of the native substrate. There were significant differences in the characteristics of the microwave- and saline water-treated cassava. Crystallinities of the microwave-treated substrates were lower than those of the saline water-treated samples. A large shift (change in 2θ) in the diffraction peaks was observed for the treated substrates as compared with the native substrate. Examination of the surface morphology suggested that saline water enabled the dissolution and elimination of the undesirable fibres in the substrate; this was not observed for the microwave-treated substrate.

Keywords: Cassava; Characterisation; Microwave; Saline water

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INTRODUCTION

Cassava mainly consists of starch, and is a source of energy for humans and animals due to its high carbohydrate content. Its composition can be changed by fermentation (Tonoukari *et al.* 2004; Gunawan *et al.* 2015; Edhirej *et al*. 2017; Hawashi *et al.* 2019). It also has small contents of fibrous compounds such as cellulose, hemicellulose, and lignin (Zhang *et al.* 2013). Cassava starch can be processed into sugar and then fermented to produce bioethanol, thereby rendering the former a renewable source of energy (Kunthiphun *et al.* 2017). This biomass is a potential raw material for bioethanol, which can be a substitute for fossil fuels (Zhang *et al.* 2013; Kang *et al.* 2014).

Bioethanol is a renewable source of energy derived from biomass and is expected to alleviate global warming. The technology for the conversion of cassava starch into

sugar and ethanol is much more established than that of cellulose. Although the technology for conversion of starch is well known, structural modification of starch by pre-treatment has drawn significant attention (Zielonka *et al.* 2012), as it is a useful approach for the production of sugar, ethanol, or value-added materials (Bodîrlău *et al.* 2014; Xu *et al.* 2016; Gryszkin *et al.* 2017; Widyorini *et al.* 2017).

In a previous study by Olanbiwoninu and Odunfa (2012), cassava was successfully pre-treated to modify its structure prior to processing it into a new material. Another study suggested that pre-treatment improved the yield of sugar by changing the chemical and physical properties of the starch (Nitayavardhana *et al.* 2008).

Methodologies involving microwave reactors and ionic liquids are sometimes called green technologies in biomass pre-treatment (Piasecka *et al.* 2014; Smuga-Kogut *et al.* 2016). Microwaves have been used in many applications, because they allow faster heating and faster chemical reactions as compared with the conventional methods (Zhu *et al.* 2006; Nomanbhay *et al.* 2013). Saline water is abundant, cheap, and safe and produces negligible waste. Ionic solutions disrupt the hydrogen bonds in biomass (Feng and Chen 2008). Microwave and ionic liquid pre-treatments improve the yield obtained from starch-based biomass such as rice, potato, and corn. The modified crystallinity of cassava has been used to improve the yields of the desired products (Mutungi *et al.* 2012).

Compounds such as synthetic ionic liquids, acids, bases, and sub-critical water (SCW) have often been employed for biomass pre-treatment (Sangian *et al.* 2015; Widjaja *et al.* 2015; Sangian and Widjaja 2017). However, these compounds have certain limitations from the viewpoints of cost effectiveness, environmental considerations, and safety considerations. It is necessary to address these limitations and develop a pre-treatment technology that is sustainable, cheap, and environmentally friendly. A comparison of the structural modification in microwave- and saline water-treated cassava has not been reported previously.

In this study, the structural changes in microwave- and saline water-treated cassava has been compared. For the pre-treatments prior to characterization, substrates were either mixed with saline water for 5 days and then dried under solar light or subjected to microwave radiation at a pre-determined power for 8 to 30 min. After the pre-treatment, the substrates were characterised by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), and scanning electron microscopy (SEM). The Miller index (*hkl*), particle size (*D*), and crystal parameters (*d*) were also determined.

EXPERIMENTAL

Chemicals and Instruments

The cassava tubers (*Manihot esculenta)* were obtained from a farmer in Minahasa, North Sulawesi, and Blitar, East Java Indonesia. They were peeled and then milled to a powdered form. The commercial salts were obtained from PT Empat Saudara, Manado, Indonesia. The first saline water was obtained from Manado beach and had a salinity of 3.43% which referred a previous report (Kalangi *et al*. 2013). To prepare saline water with a salt concentration of 10%, 100 g of salt was added to fresh water to produce one kilogram of solution.

A SHARP R-728(W)-IN microwave apparatus operating at a frequency of 2.5 GHz was used. The XRD and FTIR instruments were conducted on Panalytical X'pert

Pro (Almelo, Netherlands) diffractometer and Shimadzu PRESTIGE 21 (Tokyo, Japan) IR spectrophotometer, respectively. The surface morphology was examined using FEI Inspect S50 (Tokyo, Japan) SEM at Central Laboratory, Universitas Negeri Malang (UM), East Java, Indonesia. The XRD patterns were recorded in the 2θ range from 10.01° to 89.90°, using Kα (λ = 1.54 Å) and Kβ (λ = 1.39 Å) radiation at room temperature (25 °C), at an operating current and potential difference of 35 mA and 40 kV, respectively. The IR spectra, representing the bond vibrations, were acquired in the range of 400 to 4000 cm^{-1}. The SEM images were measured using an accelerating voltage of 15 kV and image magnification of 5000x. The working distance (WD) and the spot calibration were 10.8 mm and 5.5, respectively.

Pre-treatments

Powdered native cassava samples (250 g) were immersed in saline water at salt concentrations of 3.43% or 10% and stored for 5 days in a 1 L flask. After pre-treatment, the solid was washed with fresh water and then recovered using a funnel equipped with a filter. The substrates were dried for 2 days under solar radiation until constant weights were achieved and then stored in a plastic container. Native cassava powder with similar weights was placed inside the microwave oven and irradiated at 300 W for 10, 20, or 30 min or at 1000 W for 8 min. The substrates were characterised using XRD, SEM, and FTIR.

Determination of Chemical Compositions

For native cassava, measurements of chemical composition such as water (moisture), ash, crude fibre, fat, and protein contents were performed following the standard procedure reported by the Association of Official Analytical Chemist (AOAC) International (2003).

Calculation of Crystallinity

The Miller index was determined using a multi-step process. First, Bragg's Equation was used to determine the d_{hkl} parameter (Eq. 1), and the *hkl* values were determined using Eq. 2:

$$n\,\lambda = 2d_{hkl}sin\theta \quad (1)$$

$$\frac{l^2}{c^2} + \frac{4(h^2+hk+k^2)}{3a^2} = \frac{1}{{d_{hkl}}^2} \quad (2)$$

Here, λ and n denote the wavelength (1.5418 Å) and order (n = 1, first order), respectively; θ is the Bragg angle, and a and c are the lattice parameters. The crystallinity and particle size were determined using three equations. The Segal equation predicts the difference in intensities of I_{200} and I_{amorph} (Marimuthu *et al*. 2013) and is expressed as:

$$C = \frac{I_{200}-I_{amorph}}{I_{200}}100\% \quad (3)$$

Herman's equation was applied by Bansal *et al*. (2010); it gives the ratio of the intensity of the crystalline portion of the sample and the sum of the intensities of crystalline and amorphous portions (Eq. 4).

$$C = \frac{I_{crystal}}{I_{crystal}+I_{amorph}}100\% \quad (4)$$

The Soltys equation (Eq. 5; Nurwamanya *et al*. 2010) gives the ratio of the total crystalline area to the sum of the total crystalline and amorphous areas.

$$C = \frac{Total\ crystal\ area}{Total\ crystal+amorphous\ areas} 100\% \quad (5)$$

To determine the particle size, the Debye Scherrer equation (Eq. 6) was used, as reported by Singh *et al*. (2006):

$$D = \frac{0.9\times\lambda}{B\cos\theta} \quad (6)$$

Here, C, B, and D are the crystallinity index (%), full width half maximum (FWHM) of the diffraction band (°), and particle size (Å), respectively. $I_{crystal}$ and I_{amorph} are the crystalline and amorphous refraction intensities (Cs).

All the calculations were performed in Origin (Model 2018b, Origin Lab, MA USA) to find the exact intensity at a particular value of 2θ. Image Tool was used to determine the crystalline and amorphous areas, and Solver (Microsoft Excel) was used to determine the *hkl* parameters.

RESULTS AND DISCUSSION

Chemical Composition

Using the method prescribed by AOAC, native cassava was found to contain 81.57% starch, 1.25% protein, 0.39% lipids, 1.28% fibres, 0.26% ash, 13.74% moisture, and 1.51% other extracts. However, the substrate also contained 338.41 ppm cyanide acid, which is detrimental to human health. According to the measurement, the starch contained 17% amylose and 83% amylopectin. Since the cassava tuber has high a starch content, it can be a source for food after the removal of cyanide acid.

Crystallinity

All the treated and native samples were characterised by XRD (Fig. 1). Each sample had a distinct diffraction pattern (intensity *vs.* angle). Cassava starch had a unique peak at a specific angle, as previously reported by Harry *et al*. (2016). The substrate treated with microwave radiation at 300 W for 10 min showed peaks (and intensities (C_s), in parenthesis) at 14.91° (185), 16.99° (226), 17.91° (235), and 22.65° (221).

When the duration of irradiation was increased to 20 min, the pattern was similar, but the angles and intensities changed slightly to 15.09° (204), 16.79° (229), 17.85° (256), and 22.89° (248). Further increasing the duration of irradiation to 30 min at the same power led to a slight change in the angles but dramatic changes in the intensities (246, 313, 301, and 260 C_s).

The pattern changed when the power was increased to 1000 W. Only three peaks were observed, and their intensities decreased to 128, 130, and 126 C_s. The angles were similar to those of the samples treated at 300 W. The present findings are consistent with the results of a previous study (Singh *et al.* 2006).

The peak intensities after microwave pre-treatment at 1000 W for 8 min were the smallest compared with the three previously described conditions. The native sample showed the highest intensities and slopes for all the peaks, indicating that it has the highest degree of crystallinity (Oveanu and Nemtanu 2013; Yang *et al.* 2017).

The diffraction pattern of the native sample was different from that of the sample

treated with microwave radiation at 1000 W for 8 min, which had the least crystallinity. The XRD patterns shown in Fig. 1 were used to determine the crystalline and amorphous intensities and areas of each sample.

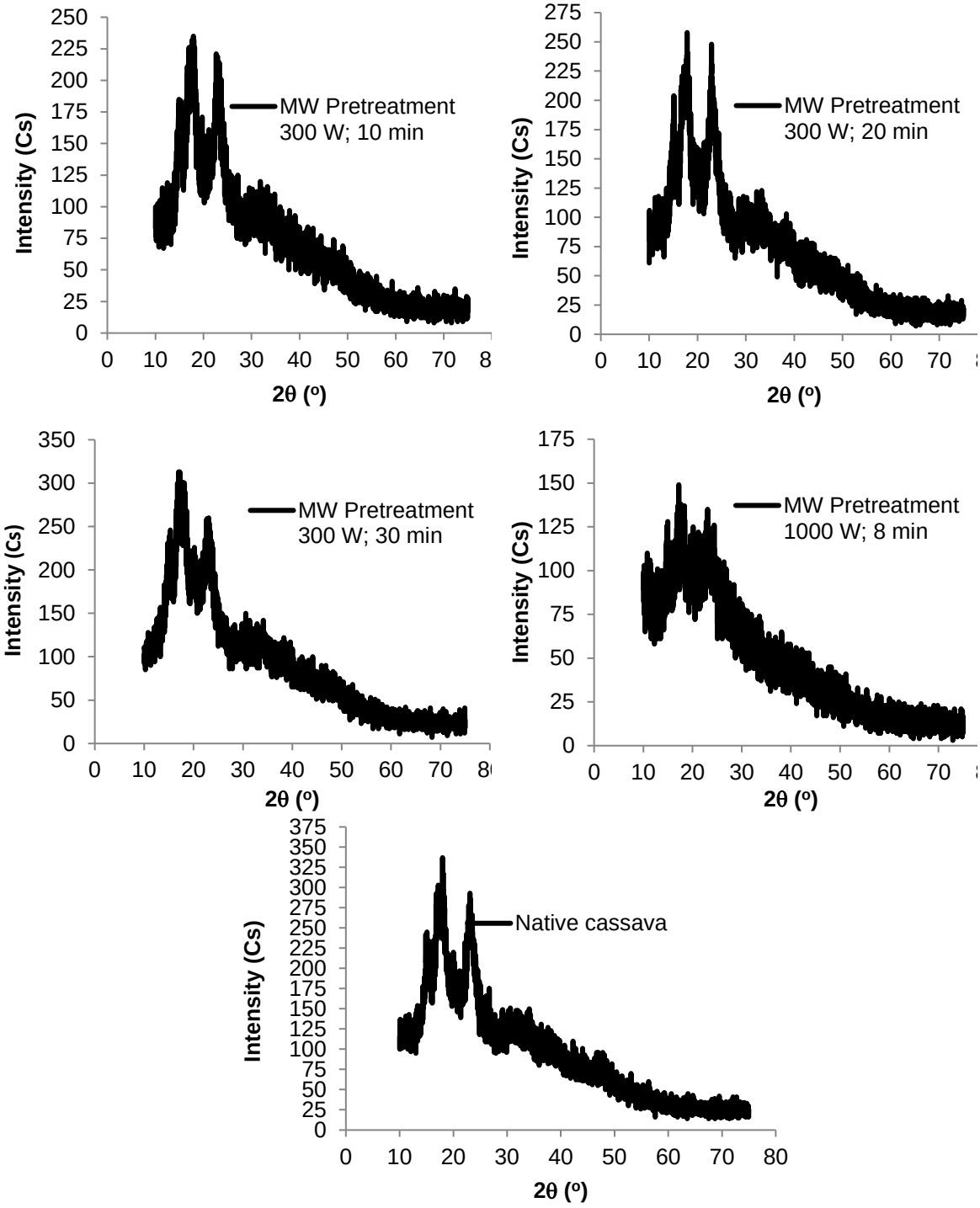

Fig. 1. XRD patterns of the native sample and substrates treated with microwave radiation (MW) at 300 W for 10 min, 20 min, or 30 min or at 1000 W for 8 min

The diffraction angles of the saline water-treated substrates were relatively close to those of the microwave-treated samples (Fig. 2). The quantities obtained from the

XRD patterns of both the microwave and saline water-treated samples were used to determine the *hkl* values and peak intensities.

The crystallinity was determined by employing the Segal, Soltys, and Hermans methods. The *hkl* indices were found using Bragg's equation, while the crystal size was calculated using the Debye Scherrer equation, after determining the FWHM values (Table 1).

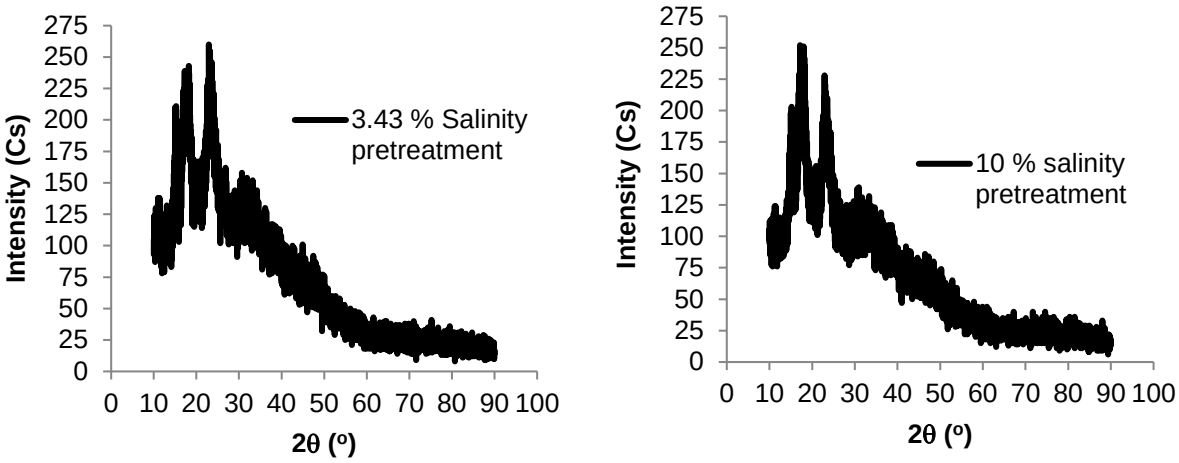

Fig. 2. XRD patterns of the substrates treated by saline water at salt concentrations of 3.43% and 10%.

The following is an example of the determination of the crystallinity of the substrate treated by microwave radiation at 300 W for 10 min, using the Segal equation. The X-ray intensities of the peak diffracted by the (200) plane and an amorphous band were determined as shown in Fig. 3. Based on the data, I_{200} was found to be 220 Cs.

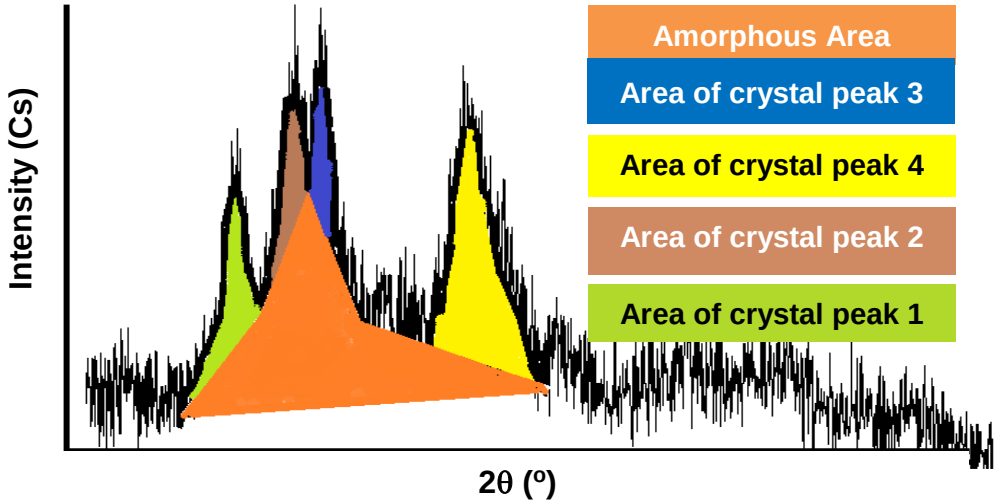

Fig. 3. Areas of the amorphous and crystalline peaks for determining the crystallinity using the Soltys equation

The intensity of the amorphous peak was determined from the intensity in the valley before the (200) plane, and it was 113 Cs. Using the Segal equation, the crystallinity of the substrate was determined to be 48.6%. This was comparable with the

value reported in a previous study on the crystallinity of saline water-treated substrates determined using another analytical method (Sangian *et al.* 2018). The Soltys Equation predicted a crystallinity of 48.0%, which is consistent with that determined using the Segal equation. The areas for each pre-treatment are listed in Table 1.

Table 1. Areas of the Crystalline and Amorphous Diffraction Bands of the Cassava Samples for All the Pre-Treatment Conditions

Pre-treatment	Area (pixels)					
	Cr. 1	Cr. 2	Cr. 3	Cr. 4	Amorph	Total
Native cassava	3666	2190	3987	10575	20758	41176
3.43% saline water	4182	3190	3610	10970	23725	45677
10% saline water	7646	5115	4749	16007	42254	75771
Microwave; 300 W, 10 min	4152	2990	3171	9998	29481	49792
Microwave; 300 W, 20 min	3592	1932	2652	8996	17620	34792
Microwave; 300 W, 30 min	3307	2660	2369	8677	19188	36201
Microwave; 1000 W, 8 min	1257	1115	1251	4451	14903	22977

The crystallinity predicted by Herman's equation (Eq. 4) was different (60.6% crystallinity). This difference is not unusual, as different methods were used for the calculations. However, the trends in crystallinity for all three methods were similar. To determine the crystallinity using Herman's equation, first, the crystalline and amorphous intensities were determined. The ratio of the total crystalline and amorphous intensities was calculated to be 60.6%. The crystallinity indices (CrI) for all the pre-treatments calculated using these equations are listed in Table 2.

Table 2. Crystallinity Indices of Native and Saline Water- and Microwave-treated Cassava

Pre-treatment	CrI (%) (Segal)	CrI (%) (Soltys)	CrI (%) (Hermans)
Native cassava	53.27	49.58	61.80
3.43% saline water	43.96	49.35	60.71
10% saline water	41.48	46.99	60.15
Microwave; 300 W, 10 min	48.63	48.05	60.63
Microwave; 300 W, 20 min	43.03	44.23	59.98
Microwave; 300 W, 30 min	38.48	40.79	59.25
Microwave; 1000 W, 8 min	26.44	39	56.17

The crystallinity of the microwave treated substrates decreased with increasing irradiation time. Using the Segal method, the CrI values of cassava treated with microwave radiation at 300 W for 10, 20, and 30 min were 48.6%, 43.0%, and 38.5%, respectively. When the power was increased to 1000 W and irradiation time was decreased to 8 min, CrI decreased to 26.4%. CrI of native cassava was 53.3%, which is comparable with the value reported in previous studies (Colman *et al.* 2014; Xie *et al.* 2013). The atomic vibrations caused by electromagnetic induction result in a disoriented particle arrangement. As the atoms oscillate for longer periods, the amorphous component of cassava becomes larger.

With the saline water pre-treatment, the crystallinity of cassava decreased as

compared with the untreated sample. The CrI values for cassava treated with 3.43% and 10% saline water, as calculated using the Segal method, were 44.0% and 41.5%, respectively. These values are consistent with a previous report (Utrilla-Coello *et al.* 2014). The decrease in CrI was similar when Soltys equation or Herman's methods were used (Table 2).

The decrease in crystallinity is influenced by electrostatic forces between the cation and anion of the salt and the hydrogen bonds and polar groups of the carbohydrate chains. The interactive force disrupts the hydrogen bonds or changes the particle orientation to a more amorphous state (Feng and Chen 2008).

Miller Index (*hkl*), Particle Size (*D*), and Crystal Parameter (*d*)

The change in crystallinity influences the particle size (*D*) of cassava, and the previously determined crystalline indices were used to calculate the Miller index (*hkl*) (Table 3). Prior to discussing the significance of these parameters, the method for determining the particle size and Miller index values is briefly described. Starch has a hexagonal structure, for which the *hkl* values can be determined using Eq. 2. By combining Eqs. 1 and 2, two equations are obtained, and the values of *A* and *C* are determined by assuming a value of $l = 0$. The Miller index (*hkl*) and the crystal size can readily be determined using the Solver software. The lattice parameter, *d*, is known from the XRD pattern.

The 2θ values were obtained using both XRD data (manual) and software calculation (*Origin*). The data show that the *hkl* values at a specific angle are similar for all the pre-treatments. For an example, the (*hkl)* values of cassava treated by saline water and microwave radiation at 2θ values of approximately 15°, 16°, 18°, and 23° were (002), (111), (200), and (202), respectively. The (*hkl*) parameters determined in this study are consistent with those in a previous report by Marimuthu *et al*. (2013).

The crystal sizes, however, are quite different for the different pre-treatments, even at similar diffraction angles. The crystal sizes of native cassava at 18° and 23° were 124.8 and 99.0 Å, respectively. The sizes changed to 166.3 and 82.5 Å when cassava was treated with 3.43% saline water. When the salt concentration was increased to 10%, the sizes at the same angles were 199.6 and 82.5 Å, respectively. Pre-treatment with microwave radiation also altered the particle sizes.

When the microwave was set at 300 W for 10 min, the crystal size at 18° was calculated to be 116.9 Å, while at 23°, it could not be calculated because the FWHM could not be determined. When the duration of irradiation was increased to 20 min at the same power, the sizes at the same angles changed to 124.8 and 99.0 Å, respectively. Thus, the particle size depended on the pre-treatment method employed, suggesting that the particle size can be changed as required (Singh *et al.* 2006).

It is thus concluded that pre-treatments do not change the (*hkl*) parameters but do affect the crystal sizes. Microwave pre-treatment for 20 min changed the crystal size, and this can be attributed to the atomic motions and vibrations over long irradiation times.

The elasticity of the substrate is lost, and the crystal size is higher than that of native cassava. The particle sizes for samples subjected to microwave pre-treatment at 300 W for 30 min and 1000 W for 8 min could not be obtained as the FWHM values were difficult to measure from the XRD patterns. This was probably because these substrates were much more amorphous compared with that of the untreated sample.

Chemical Bond Analysis

Native cassava was treated with microwave radiation at 300 W for 10, 20, or 30 min or at 1000 W for 8 min, and the native and treated substrates were characterised by FTIR. The spectra were acquired in the range 400 to 4000 cm^{-1} (Fig. 4).

The transmittance of the substrates treated with microwave radiation at 300 W for 10 and 20 min was similar to those of the untreated sample in the range 300 to 2000 cm^{-1}. Beyond this region, the transmittance of the pre-treated samples decreased relative to the untreated sample.

Table 3. Miller Indices and Particle Sizes of Cassava for All the Pre-treatments

Pre-treatment	2θ (°)		(*hkl*)	*d* (Å)	*D* (Å)
	Manual	Origin			
Original cassava	15.16	15.09	002	5.86	125.20
	16.98	17.19	111	5.15	166.57
	17.98	18.11	200	4.89	124.75
	23.04	23.09	202	3.84	99.01
3.43% saline water	15.20	15.25	002	5.80	125.20
	17.11	17.27	111	5.13	166.54
	18.12	17.99	200	4.92	166.31
	23.13	22.93	202	3.87	82.50
10% saline water	15.12	15.19	002	5.82	143.12
	17.00	17.17	111	5.16	166.57
	18.06	18.01	200	4.92	199.59
	23.10	22.91	202	3.88	82.50
Microwave; 300 W, 10 min	15.02	14.91	002	5.93	125.22
	17.10	16.99	111	5.21	102.42
	17.94	17.91	200	4.94	116.92
	-	22.65	202	3.92	-
Microwave; 300 W, 20 min	15.06	15.09	002	5.86	166.97
	16.83	16.79	111	5.27	166.61
	17.88	17.85	200	4.96	124.77
	22.93	22.89	202	3.88	99.03
Microwave; 300 W, 30 min	15.09	15.29	002	5.85	100.17
	17.11	17.21	111	5.20	99.92
	18.18	17.91	200	4.98	124.71
	22.99	23.01	202	3.86	123.77
Microwave; 1000 W, 8 min	15.11	14.97	002	5.91	68.45
	-	17.3	111	5.12	-
	-	-	-	-	-
	-	23.07	202	3.85	-

Thus, the structures of cassava treated with short microwave radiation were slightly different. When the irradiation time was increased to 30 min, the transmittance increased, indicating that more photons passed through the substance.

The interaction between infrared waves and molecules or atoms decreases, thereby decreasing the energy absorbed. When the microwave power was increased to 1000 W and irradiation time was decreased to 8 min, the transmittance increased compared with the untreated substrate. The peak around 3500 cm^{-1} almost disappeared, indicating that a portion of cassava has been damaged. This is also consistent with the other observations in this study.

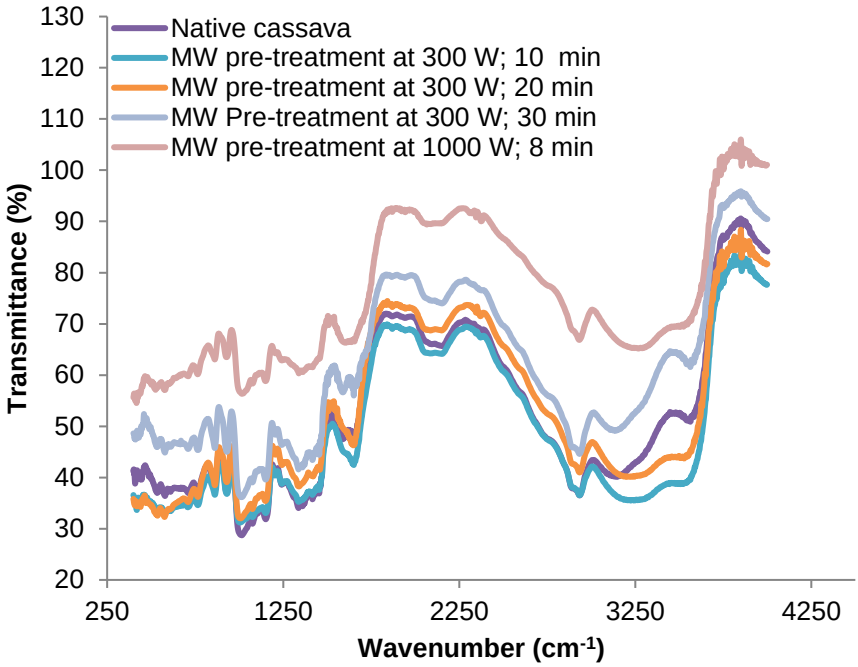

Fig. 4. Comparison of the FTIR spectra of native cassava and cassava treated with microwave (MW) radiation at 300 W for 10, 20, and 30 min and at 1000 W for 8 min.

The substrate treated with microwave irradiation at 1000 W for 8 min had a blackish, coffee-like colour. The substrates treated at 300 were light brownish in colour. The change in transmittance can be explained by weakening of the chemical bonds in the starch and damage to the dextran chains by high-frequency vibration. The change in transmittance is expected because of the change in crystallinity of the treated sample (Kizil *et al.* 2002; Xie *et al.* 2013).

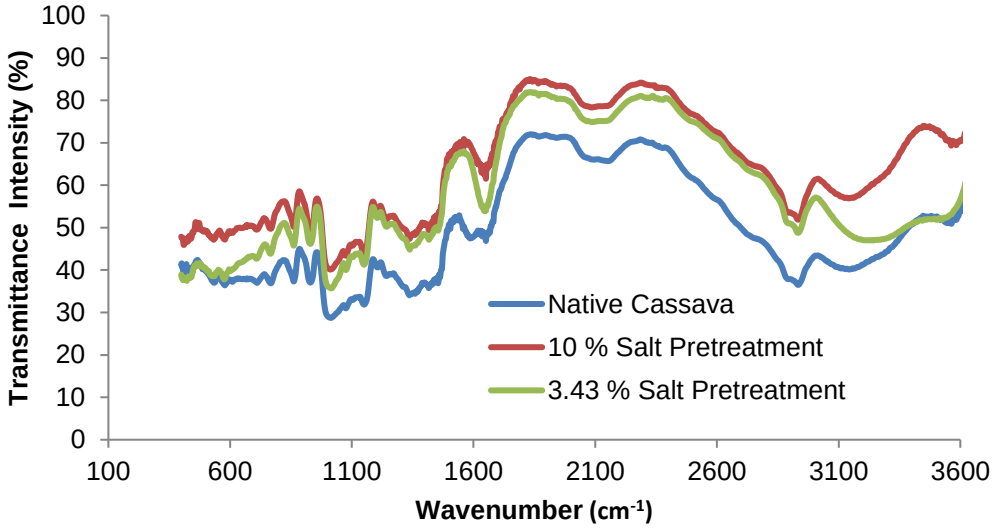

Fig. 5. FTIR spectra of cassava powder pretreated with 3.43% (red line) and 10% saline water (grey line) and native cassava powder (blue line)

Table 4. Absorbance and Functional Group Assignments for Native Cassava, Cassava Treated with Microwave Radiation at 300 W for 10, 20, and 30 min and at 1000 W for 8 min, and Cassava treated with Saline Water at Salt Concentrations of 3.43% and 10%

Wavenumber (cm^{-1})	Absorbance							Functional Group Vibration**
	MW pre-treatment 300 W			1000 W	Saline water pre-treatment			
	10 min	20 min	30 min	8 min	Untreated	10%	3.43%	
530.42-707.88	0.48	0.49	0.34	0.24	0.43	0.33	0.41	C-C-O bending And C-O torsion
	0.48	0.49	0.35	0.24	0.44	0.33	0.42	
	0.47	0.45	0.34	0.22	0.43	0.30	0.37	
765.74-862.18	0.46	0.44	0.34	0.22	0.43	0.30	0.36	C-C stretching; C(1)-H, CH_2OH
	0.44	0.41	0.34	0.20	0.43	0.30	0.34	
929.69-1076.2	0.43	0.41	0.35	0.20	0.43	0.31	0.34	C-O-C C-O-H; C-OH and CH_2 deformation
	0.51	0.49	0.44	0.25	0.54	0.40	0.45	
	0.49	0.47	0.41	0.23	0.50	0.36	0.40	
1149.5-1203.5	0.48	0.45	0.40	0.23	0.50	0.35	0.38	C-O-C antisymmetric; C-C, C-O stretching
	0.39	0.35	0.32	0.20	0.39	0.27	0.28	
1242.1-1336.6	0.41	0.37	0.33	0.20	0.41	0.28	0.30	CH_2OH
	0.45	0.42	0.38	0.23	0.47	0.32	0.35	C-O-H
2933.7-3167.1	0.44	0.39	0.35	0.17	0.44	0.28	0.3	C-H and O-H stretching
	0.45	0.39	0.31	0.18	-	-	-	

*Absorbance, A, was determined using the formula $A = -\log(T/100)$.
** Kizil *et al.* 2002; Bergo *et al.* 2010; and Garrido *et al.* 2014.

Table 4 lists the absorbance and functional group assignments for the microwave- and saline water-treated cassava based on the FTIR spectra. For both the pre-treatments, bands corresponding to the functional group were found in the same region. C-C-O bending, for example, occurred at 530.42 and 576.72 cm^{-1} for the microwave treated sample, and at 536.2 and 578.6 cm^{-1} for the saline water treated sample. C-C stretching was observed at 765.74 cm^{-1} (microwave) and 767.70 cm^{-1} (saline water). The C-H and O-H stretching motions were for the microwave-treated samples were observed at 2933.7 and 3167.1 cm^{-1}, while for the samples pre-treated with saline water, only the C-H stretching motion at 2935.7 cm^{-1} was observed (Fig. 5).

The data indicated that the absorbances of the cassava samples for both the pre-treatments were relatively high at lower wavenumbers. As the frequencies absorbed by the microwave- and saline water-treated cassava were different from those of the native substrate, it is clear that the structures of the samples were modified by pre-treatment. The relatively small changes observed in the FTIR and XRD spectra of the treated samples indicated that the chemical structure of the native cassava remained intact for most parts in the treated samples, and therefore, the pre-treatments had a more pronounced effect on the physical structure of the samples.

Surface Morphology

The surface morphology of native cassava and microwave- and saline water-treated cassava were examined using SEM (Fig. 6). It is very important to obtain information about the surface of the cassava samples. The SEM images showed that impurities in the cassava samples were not eliminated by microwave irradiation.

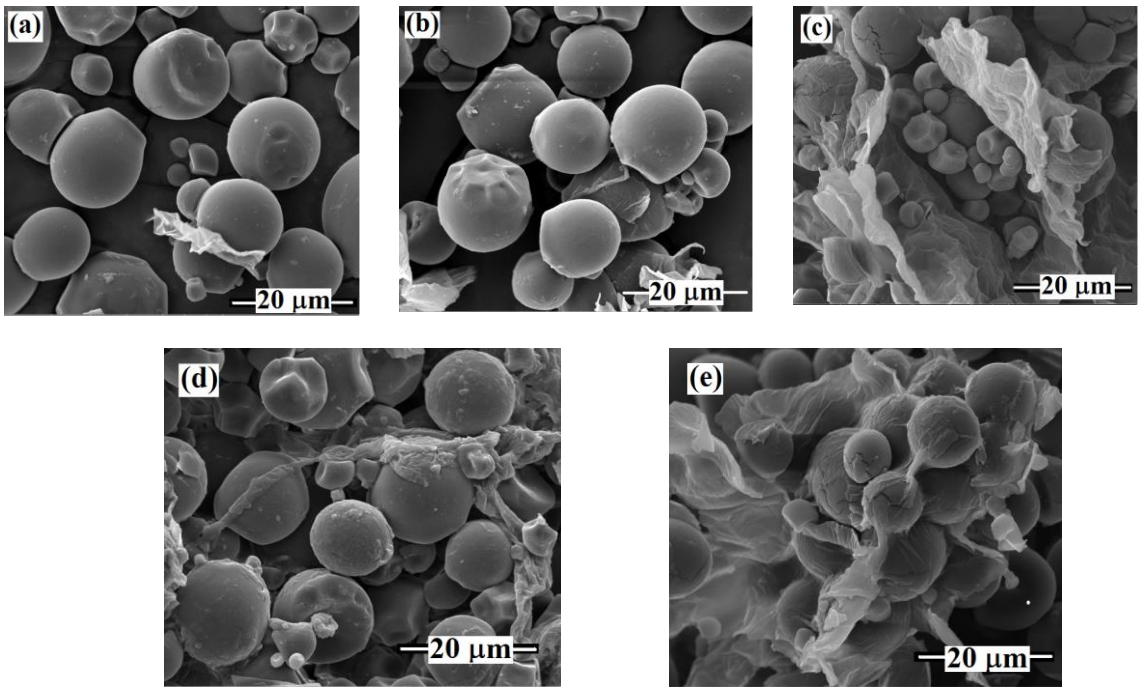

Fig. 6. Surface morphologies (5000x magnification) of cassava treated with microwave radiation at 300 W for 10 min (a), 20 min (b), and 30 min (c) and at 1000 W for 8 min (d). Morphology of the untreated sample (e)

Microwave irradiation changes the surface morphology of the substrate, and the distance between the particles are higher than that in the untreated samples (Xie *et al.* 2013). This indicates that the treated substrates were more porous, and many fibres were broken. When the substrates were treated with saline water, the amount of fibres connecting the starch particles were reduced significantly, as shown in Fig. 7. The salt, which ionises into cations and anions, interacted with the OH groups connecting the other fibres and starch. This interaction led to the dissolution of some of the fibres and starch (Feng and Chen 2008). When the solids were washed and recovered, some impurities were left behind in the saline water. In the sample subjected to 3.43% salt pre-treatment, the amount of impurities was reduced. When the salt concentration was increased to 10%, the impurities were almost eliminated from the cassava sample.

It is clear from the images that the particle shapes were altered after pre-treatments. While the original starch particles were mostly spherical, elliptical, or irregularly shaped without defects, similar to that observed in a previous study (Perez and Bertoft 2010), microwave pre-treatment changed the particle shapes significantly. Microwave irradiation at 300 W for 10, 20, and 30 min (or at 1000 W for 8 min) damaged and fractured the particles, which could be caused by the rapidly increasing temperature inside the substrate owing to the induction of electromagnetic waves (Deka and Si 2016).

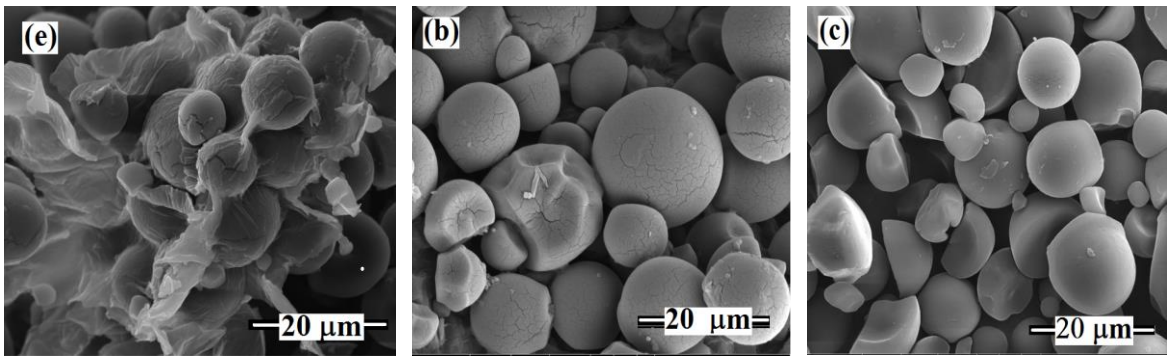

Fig. 7. Surface morphologies (5000x magnification) of native cassava (a) and cassava treated with saline water at salt concentrations of 3.43% (b) and 10% (c)

The shapes of the particles of the saline water treated samples were relatively different from those of the microwave pre-treated samples. The particle surfaces of the saline water-treated sample were smother and clearer and had no impurities. This was in contrast to the previous samples. After pre-treatment, many particles were destroyed, and swelling was observed for a small fraction. This could be attributed to the penetration of saline water inside the substrate. The particles that were not destroyed were mostly spherical. Increasing the concentration of saline water increased the number of fractured particles.

Microwave and saline water pre-treatments result in a different particle distribution, as shown in the images. The distribution of microwave treated particles at both 300 W and 1000 W, for all the time duration, was more spacious compared with that of the saline water pre-treatment, in which the particle were more compact. Since the particles were more compact, the density of saline water treated sample was higher than that of the microwave treated sample. The sample treated with saline water occurred an agglomeration/fusion. This behaviour was consistent with that reported in a previous work (Kärkkäinen *et al.* 2011).

The images show that microwave pre-treatment influenced the particle sizes. Some of the particles underwent volume expansion or were swollen, while and the rest became smaller as they were destroyed. The particle sizes of the sample treated with 3.4% saline water were higher compared with that of native cassava. At 10% salinity, however, the starch size was remarkably small. It was found that increasing salinity increased the destruction of particles into smaller sizes.

CONCLUSIONS

1. Cassava was pre-treated with microwave radiation or saline water.
2. Microwave irradiation and saline water changed the structure of the cassava samples, as indicated by the crystallinity values obtained from the XRD measurements.
3. When the microwave power or salt concentration in the saline water was increased, the crystallinity values decreased compared with that of native cassava. The CrI trends for both the pre-treatment methods were similar.

4. The functional groups detected by FTIR for both the pre-treatments were relatively similar, but the vibrational frequencies were different.
5. Saline water could eliminate the fibres in the cassava samples. In contrast, the microwave pre-treatment only changed the surface morphology, without reducing the amount of undesirable fibres.

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