ORIGINAL ARTICLE

Study of the Effects of Ultraviolet Light and Sodium Hypochlorite Solutions on Properties of Cassava Starch Granules

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Abstract In this study, samples of native cassava starch were oxidised with standard NaClO solutions (0.1, 0.2 and 0.5 mol L^{-1}) and exposed for 1 h under UV light (UVC radiation with $\lambda=256$ nm); they were subsequently filtered, washed, dried and analysed. The thermogravimetric curves showed similar behaviour, with three main mass losses and a decrease in the thermal stability for samples (1) and (3). The oxidative modification performed caused a decrease in the viscosity peaks (RVA), gelatinisation enthalpy (DSC) and relative crystallinity (XRD), and an increase in the average roughness (NC-AFM). The X-ray diffraction powder patterns displayed the "A" type for all the starch granules. The colour parameters showed a slight increase in the L* value (trend to white) for the treated samples.

Keywords Cassava starch · Sodium hypochlorite · Oxidised starch · Ultraviolet light · Thermal analysis

Introduction

Cassava root (*Manihot esculenta* C) contains 60–70 % water, 30–40 % carbohydrates, 15–33 % starch, which varies with the maturity of the root and climatic conditions, 2.6 % proteins, 2.7 % fibre and 0.3 % lipid content [1]. Starch has

singular technological properties that allow its use in several industrial applications. Among these properties are the non-existence of the typical "cereal flavour" of corn and other cereal starches, its capacity for a higher degree of swelling during cooking, and lower pasting temperature. Its low protein and lipid contents must also be considered, which contribute to its neutral flavour and white colour [2].

Starch is a semi-crystalline polymer and it is principally composed of two macromolecules: amylose and amylopectin, which represent approximately 98–99 % of the dry weight. These glucose polymers are found inside vegetable cells. Amylose is predominantly a linear polymer of α-1.4 linked glucose, whereas amylopectin is a highly branched polysaccharide consisting of α-1.4 linked glucose with α-1.6 linkages at the branch points. These macromolecules are extracted, among many others, for use in the food, paper, chemical, pharmaceutical and textile industries [3–5].

In their native forms, starches generally do not have suitable physical or chemical characteristics for certain types of industrial processing. Some of these characteristics include shear resistance, water insolubility and synerisis, which in some cases make them complex to use [6]. Starches can be modified by chemical, physical, enzymatic or combined methods. Oxidative modification has been subject of much research; it is mainly used to produce starch pastes with more fluidity and cohesion and whiter granules, as well as more transparent pastes [2, 7].

Hypochlorite oxidation is the oldest and most popular commercial method for the production of oxidised starches on an industrial scale [7]. The ultraviolet irradiation of starch leads to depolymerisation and, depending on the wavelength and intensity, the treatment may afford dextrins, monosaccharides, oligosaccharides, water and carbon dioxide [8]. A study in the relevant literature [9] found that the treatment of starch with UV light induced changes in its functional properties, such as

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increased water binding capacity and solubility, and decreased hot paste viscosity.

In this study, we examined the effects of oxidative modification on native cassava starch for 1 h under the double and simultaneous action of UV light and sodium hypochlorite solutions at different concentrations. The main properties of modified and native starches were evaluated using thermal analysis, X-ray diffractometry, rheological and microscopic analysis.

Materials and Methods

Origin and Modifications of the Starch

The native cassava starch (500 g) for this study was bought in the local commercial market of Ponta Grossa, PR, Brazil. The starch was divided into four parts of 50 g (dry basis). One of these was maintained as received and was designated the (N) native or untreated sample; the other three samples were treated following the literature methodology [10, 11] with modifications. The cassava starches were treated with standard sodium hypochlorite (NaClO) solutions for 1 h of exposure in ultraviolet light (λ=256 nm). For samples 1, 2 and 3, 0.1, 0.2 and 0.5 mol.L^{-1} of NaClO was used, respectively The modified samples were then washed and filtered until the complete elimination of ClO^{-} ions. The samples were dried in an oven with forced air circulation for 24 h at 40 °C and then analysis was performed.

Thermogravimetric Study (TG/DTG)

The TG/DTG curves were obtained using a thermal analysis system (Shimadzu, TGA-50 model, Japan); the samples were heated from 35 °C to 650 °C using open alumina crucibles with approximately 5.0 mg of the sample under a synthetic air flow of 150 mL.min^{-1} at a heating rate of 10 °C min^{-1}. The instrument was preliminarily calibrated with standard weight and with standard calcium oxalate monohydrate. All mass loss percentages were determined using TA-60 WS data analysis software. The derivative thermogravimetric curves (DTG), the first derivative of the TG curves, were calculated [11, 12].

Differential Scanning Calorimetry (DSC)

The DSC curves were obtained using a thermal analysis system (TA-Instruments, DSC-Q200 model, USA). The DSC curves were recorded under an air flow of 50 mL.min^{-1}, heating rate of 10 °C min^{-1} and the samples weighed about 2.5 mg. A 4:1 (water:starch w/w) mixture was prepared and maintained for 60 min in order to equilibrate the moisture content. The aluminum crucibles were sealed and then the curves were performed. The instrument was previously calibrated with 99.99 % purity Indium, melting point of $T_{p.}$=156.6 °C, ΔH=28.56 J.g^{-1} [11, 12].

Rapid Viscoamylographic Analysis (RVA)

The pasting properties of the samples were obtained by using a viscometer (Newport Sci., RVA-4 model, Australia). A suspension of 3.0 g of starch in 25.0 g of distilled water underwent a controlled heating and cooling cycle under constant shear where it was held at 50 °C for two min, heated from 50 to 95 °C at 6 °C min^{-1}, held at 95 °C for 5 min, cooled to 50 °C at 6 °C min^{-1} and held at 50 °C for 2 min [12, 13].

Atomic Force Microscopy (AFM)

The micro-images of each sample were observed with high resolution using an atomic force microscope (Shimadzu, SPM-9600 model, Japan) using the non-contact method (NC-AFM). All the measurements were performed in triplicate and this technique allowed us to observe the surface of the studied starches and also to calculate the average diameter and the average roughness of the samples [11, 12, 14, 15].

X-ray Diffraction Powder Patterns (XRD)

The X-ray diffraction powder patterns (XRD) were obtained by using an X-ray diffractometer (Rigaku, Ultima 4 model, Japan), employing Cu Kα radiation (λ=1.541 Å) and settings of 40 kV and 20 mA. The scattered radiation was detected in the angular range of 5–50° (2 θ), with a scanning speed of 8° min^{-1} and a step of 0.06°. The degree of relative crystalinity was quantitatively estimated using Equation 1 and the method followed was as described in the literature [11, 12, 14, 15].

$$Xc = \frac{Ap}{(A_p + Ab)} . 100 \qquad (1)$$

Colour Parameters

To determine the colour parameters of the samples before and after treatment was used a MiniScan XE reflectance spectrophotometer 45/0-L Plus (Hunter Inc., USA), which consists of three colour components: L^*, a^* and b^*, followed as in the literature [12]. The L^* represents brightness ranging from 0 (black) to 100 (white); a^* ranging from positive (red) to negative (green); and b^* ranging from positive (yellow) to negative (blue).

Statistical Analysis

The normality of experimental data was tested by Shapiro-Wilk test ($p > 0.05$ was considered normal) and to

homogeneity of variance was used Brown-Forsythe test ($p>0.05$ was considered homoscedastic). To the data that didn't follow a normal distribution, the Box-Cox transformation was used. Then normal and homoscedastic data were evaluated by analysis of variance (ANOVA) complemented with Fisher LSD post-hoc test. A value of $p\leq0.05$ was considered significant. A value of $p>0.05$ was considered not significant and the Fisher LSD post-hoc test was not used [16]. Statistical analyses were performed by Statistica software version 8.0 (Statsoft, Tulsa OK, USA).

Results and Discussion

TG/DTG

The thermogravimetric curves (TG/DTG) of the untreated sample (N) and the modified samples (1, 2, 3) of cassava starch were performed and it was possible to verify that the profile of each curve showed three main mass losses. Three distinct regions were observed on the TG/DTG curves: the first region began at room temperature up to around 160 °C, which represents the evaporation of the water and volatile compounds, followed by stability. Once dehydrated, the second and third main regions in the TG curves were due to the degradation of the organic matter (amylose) and the formation of final residue (ash), which was 0.96, 0.63, 0.90 and 0.77 % of the initial mass of each sample, respectively. The initial mass of the samples were (N) 5.06, (1) 5.15, (2) 5.12, (3) 4.87 mg, respectively. All the TG/DTG curves are shown in Fig. 1 and the results are shown in Table 1.

Comparable thermogravimetric curves were reported in earlier studies of cassava starch granules treated with hydrochloric acid [4]; natural and modified cassava starch treated with sodium hypochlorite [2]; organic cassava starch treated with heat moisture [13]; and cassava starch treated with microwave [12]. In addition, there have been studies of starches from other botanical origins, such as *pinhão* (*Araucaria angustifolia*), starch from different germoplasm origins [17], potato starch from different cultivars [18], and oxidised starch from Peruvian carrots [19].

DSC

The DSC curves were performed in order to study the gelatinisation process and they were obtained at a low heating rate (10 °C min^{-1}) in the proportion of 1:4 starch:water, in sealed aluminum crucibles. Figure 2 shows the profile of the DSC curves.

Table 2 depicts the obtained DSC results. As can be seen, when compared with the (N) native cassava starch sample, the peak temperatures (T_p), showed a slight decrease for samples (2) and (3) and an increase for sample (1). The calculated
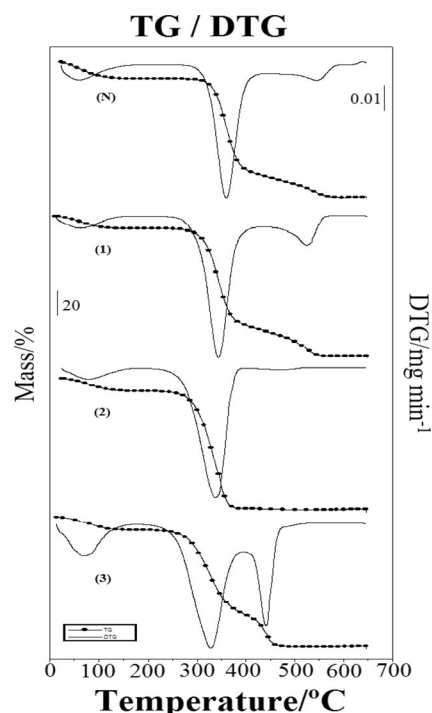

Fig. 1 TG/DTG *curves*: (N) native cassava starch; (1; 2; 3) native cassava starch treated with UV-light ($\lambda=256$ nm) at 1 h exposure and NaClO standard solutions 0.1; 0.2 and 0.5 mol L^{-1}, respectively

gelatinisation enthalpy (ΔH_{gel}) showed a strong decrease in contrast with the result observed for the (N) sample. Similar values for enthalpy were found in the literature [12, 13, 20];

Table 1 TG and DTG results of: (N) native cassava starch; (1; 2; 3) native cassava starch treated with UV-light ($\lambda=256$ nm) at 1 h exposure and NaClO standard solutions 0.1; 0.2 and 0.5 mol L^{-1}, respectively

Samples	TG results		DTG results	
	Step	Δm/%	ΔT/°C	T_p/°C
(N)	1st	10.87	30–188	63.73
	Stability	–	188–294	–
	2nd	72.88	294–453	362.61
	3rd	15.29	453–609	548.92
(1)	1st	8.47	30–185	82.67
	Stability	–	185–253	–
	2nd	71.86	253–426	354.13
	3rd	19.03	426–598	532.19
(2)	1st	9.22	30–205	82.42
	Stability	–	205–341	–
	2nd	88.03	341–422	341.25
	3rd	1.84	422–628	473.14
(3)	1st	9.15	30–161	74.45
	Stability	–	161–268	–
	2nd	64.97	268–397	332.00
	3rd	25.71	397–596	444.62

Δm mass loss (%), ΔT temperature range, T_p peak temperature
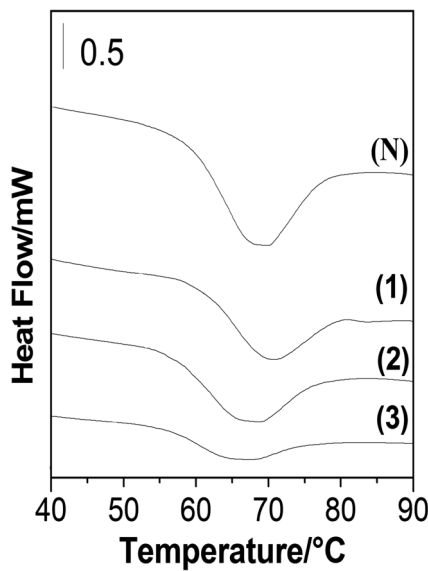
Fig. 2 DSC gelatinization curves: (N) native cassava starch; (1; 2; 3) native cassava starch treated with UV-light (λ=256 nm) at 1 h exposure and NaClO standard solutions 0.1; 0.2 and 0.5 mol L^{-1}, respectively

the values obtained, for esterified cassava starch with long alkyl side chains and different substitution degree, for cassava starch treated with heat-moisture, and for cassava starch exposed to microwave radiation were 7.20, 7.31 and 9.14 J.g^{-1}, respectively. Other authors [11] found values of 16.2, 17.0 and 22.4 J.g^{-1} for ΔH_{gel} of cassava starch treated with NaClO at 0.8, 2 and 5 %, respectively. Other research [21] found ΔH_{gel} values of 14.1 to 17.4 J.g^{-1} for untreated and NaClO-oxidised cassava starch at different reaction times. Lower enthalpy values than those observed in the present study were found in the literature [22]. These were 4.44, 3.09, 2.91 and 2.46, respectively, for untreated avocado starch and for avocado

starches treated with NaClO (0.5, 1.0 and 2.0 %). These differences between the results were due to the different treatments that were performed (reagent concentrations, time of treatment, genetic varieties, physical methods of treatments).

RVA

The RVA results are shown in Fig. 3 and Table 3. A moderate decrease in the viscosity peak (3870 cP for the (N) sample) occurred for the oxidised samples; sample (1) 1414 cP, which showed the lowest value; sample (2) 2386 cP; and sample (3) 1576 cP. In research [23] about the effects of different UV irradiations on properties of cassava starch, similar behaviour was found for oxidised starches in terms of viscosity peaks. In addition, even lower values can be observed for final viscosity for each sample, Similar occurrences were found in research about the molecular properties of cassava starch that was modified with different UV irradiations [24].

According to research [25], during the oxidation process the hydroxyl groups of starch molecules are oxidised to carbonyl groups, followed by carboxyl groups, which alter the molecular structure and properties, as observed in the present study. A direct correlation can be observed between peak viscosity (RVA) and gelatinisation enthalpy (DSC).

The method of modification applied in this study, strongly decreased the seatback results for the modified samples as can be observed in Fig. 3 and Table 3. Pastes with low results for seatback, are required to the bakery food industry, which are related to a less tendency to the retrogradation event. The main properties affected by a strong retrogradation process is deterioration of texture of bakery products and on water loss (syneresis) of starch based deserts [26].

Table 2 DSC gelatinization, NC-AFM and XRD results of: (N) native cassava starch; (1; 2; 3) native cassava starch treated with UV-light (λ=256 nm) at 1 h exposure and NaClO standard solutions 0.1; 0.2 and 0.5 mol L^{-1}, respectively

Samples	DSC gelatinisation			AFM			XRD
	To/°C	Tp/°C	Tc/°C	ΔH_{gel}/J.g$^{\pm1}$	d_a/μm	r_a/nm	Degree of relative cristallinity
(N)	59.31±0.07[b]	68.32±0.02[b]	70.58±0.01[b]	11.01±0.49[a]	11.34±2.93	421.31±0.30[a]	24.53±0.30 [a]
(1)	61.69±0.07[a]	69.99±0.03[a]	79.05±0.65[a]	6.68±0.53[b]	12.39±5.98	395.05±0.03[b]	22.32±0.99[b]
(2)	57.28±0.08[c]	66.58±0.09[c]	69.42±0.07[c]	7.09±0.40[b]	11.44±1.72	279.07±0.03[d]	21.43±0.82[b]
(3)	56.70±0.53[d]	65.69±0.90[d]	68.77±0.60[c]	5.69±0.73[c]	11.88±2.67	375.14±0.03[c]	21.42±0.99[b]
p (Shapiro-Wilk)**	0.05	0.14	0.05	0.51	0.19	0.06	0.52
p (Brown-Forsyth)**	0.45	0.49	0.12	0.40	0.18	0.29	0.85
p (Anova)***	0.00	0.00	0.00	0.00	0.96	0.00	0.00

(*) To "onset" initial temperature, Tp peak temperature, Tc "endset" final temperature, ΔH_{gel} gelatinization enthalpy, (d_a) Average diameter, (r_a) Average roughness, the degree of crystallinity was calculated as a percentage, peaks are determined in 2θ, (**) Probability values obtained second Shapiro-Wilk test for normality and Brown-Forsythe test for homogeneity of variances, (***) Probability value obtained second analysis of variance (ANOVA), (****) Different letters in the same column represents significative difference according to Fisher LSD test (p<0.05)
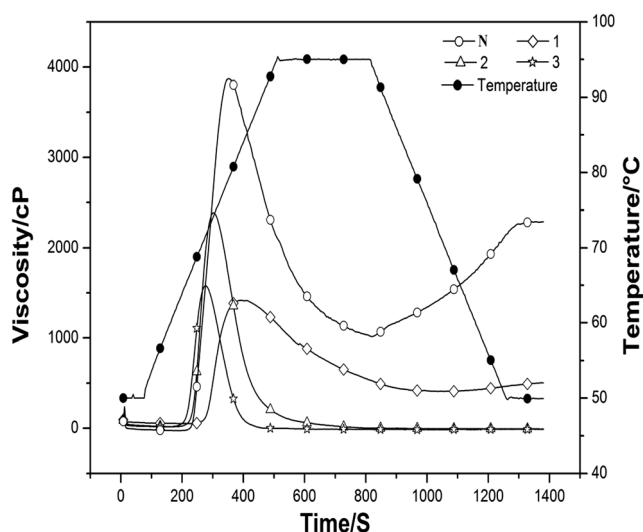
Fig. 3 RVA *curves*: (N) native cassava starch; (1; 2; 3) native cassava starch treated with UV-light (λ=256 nm) at 1 h exposure and NaClO standard solutions 0.1; 0.2 and 0.5 mol L^{-1}, respectively

AFM

The micro-images of the starch granules before and after the treatment were observed using the non-contact method of atomic force microscopy (NC-AFM) and these are shown in Fig. 4. The average diameter (d_a) and average roughness (r_a) were calculated. The highest average diameter, as well as the highest average roughness was observed from sample (1) (12.39 and 395.05 μm, respectively). All the results are shown in Table 2. Another study in the literature [13] found similar values for roughness.

The micro-images of the starches granules presented in Fig. 4 show granules with slight roughness for the (N) sample and with few fissures on the surface. However, as the concentration of the reagent (NaClO) increased, the roughness and the fissures on the surface granules also increased for the treated samples. In other research [20], the authors found the

same behaviour for untreated and NaClO-oxidised cassava starch granules.

X-rayDiffractometry

Figure 5 shows the X-ray diffractograms for each sample. Literature reports [27, 28] suggest that, according to their main peaks and diffractograms patterns, starch granules present the following classification: type "A", when the main peaks are shown in 15, 17, 18 and 23° into 2 θ; type "B", in 5.6; 15, 17, 18 and 23° into 2 θ; and type "C", which is considered as a mixture between the values 5.5; 15, 17, 22 and 23° into 2 θ. According to [29], many tuberous starches, such as cassava starch, are classified as "A" or "C" or even "AC".

The main diffraction peaks are shown, which were at approximately 2 θ 15, 17, 18 and 23° and which had no displacements; these peaks showed the characteristic "A" pattern of cereal starches [27–29]. The calculated degrees of relative crystallinity, using Equation 1 according to the literature [12, 13], were 24.53, 22.32, 21.43 and 21.42 %, respectively, for the samples (N), (1), (2) and (3) and these are shown in Table 2. It can be observed that there was a slight decrease in crystallinity when the reagent concentration increased in the treated samples, compared with the (N) sample.

Colour Parameters

Table 4 shows the colour parameters for the native and treated samples.

Three parameters of colour were evaluated: L*, a* and b*. The L* value denotes brightness, ranging from white (L*= 100) to black (L*=0). The a* value characterises the colour in the region of red (+a*) to green (−a*). The b* value indicates the colour range from yellow (+b*) to blue (−b*) [12]. Table 4 shows that a slight difference in the L* value (trend to white) occurred between the untreated sample and the treated

Table 3 RVA results of: (N) native cassava starch; (1; 2; 3) native cassava starch treated with UV-light (λ=256 nm) at 1 h exposure and NaClO standard solutions 0.1; 0.2 and 0.5 mol L^{-1}, respectively

Samples	Pasting temperature/°C	Viscosity peak/cP	Peak time/sec	Setback/cP	Break/cP	Final viscosity/cP
(N)	66.25±0.07[b]	3,870±0.71[a]	5.86±0.01[b]	1,274±0.71[a]	2,858±0.71[a]	2,286±0.71[a]
(1)	71.13±0.02[a]	1,414±0.71[d]	6.52±0.01[a]	94±0.71[b]	1,006±0.71[d]	502±0.71[b]
(2)	65.83±0.03[c]	2,386±0.71[b]	5.08±0.01[c]	−2.5±0.71[d]	2,394±0.71[b]	−9.5±0.71[c]
(3)	64.20±0.14[d]	1,576±0.71[c]	4.62±0.01[d]	3.5±0.71[c]	1,594±0.71[c]	−13±0.71[d]
p (Shapiro-Wilk)**						
p (Brown	0.07	0.06	0.86	0.05	0.05	0.05
Forsyth)**	0.69	0.54	0.66	0.19	0.48	0.12
p (Anova)***	0.00	0.00	0.00	0.00	0.00	0.00

(*) cP "centipoises", sec "seconds", (**) Probability values obtained second Shapiro-Wilk test for normality and Brown-Forsythe test for homogeneity of variances, (***) Probability value obtained second analysis of variance (ANOVA), (****) Different letters in the same column represents significative difference according to Fisher LSD test (p<0.05)

Fig. 4 Micro-images: (N) native cassava starch; (1; 2; 3) native cassava starch treated with UV-light (λ=256 nm) at 1 h exposure and NaClO standard solutions 0.1; 0.2 and 0.5 mol L^{-1}, respectively
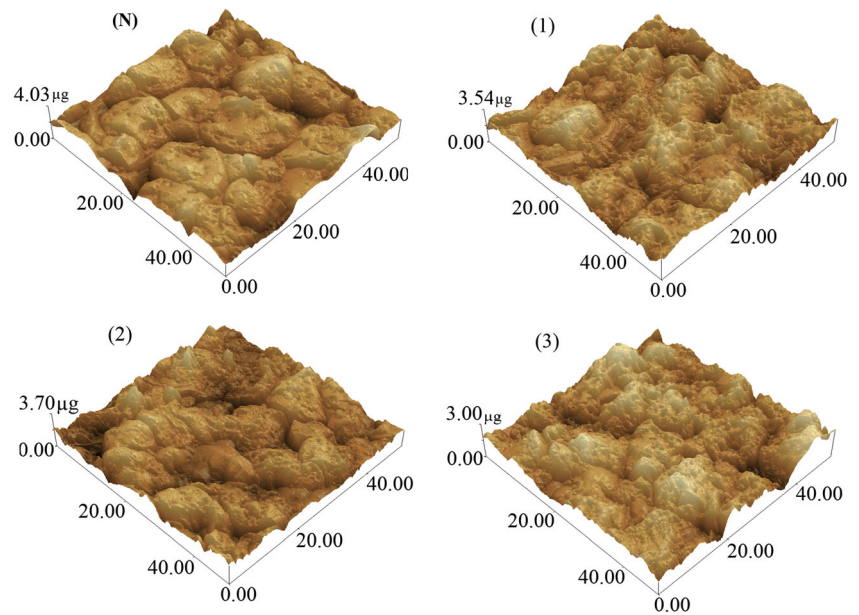
samples, it can be said that the reagent concentration wasn't high enough to cause a brightening effect. The b* value (trend to yellow) decreased considerably from the (N) sample to sample (1) and also the -a* (trend to green) from the (N) sample to samples (1) and (2) increasing strongly to (3) one. These results are not perceived by human eyes. These analysis of colour is required, for example, by the paper, textile, laundry finishing, building materials and food industries that requires oxidized starches to provide clarity to the products [30].
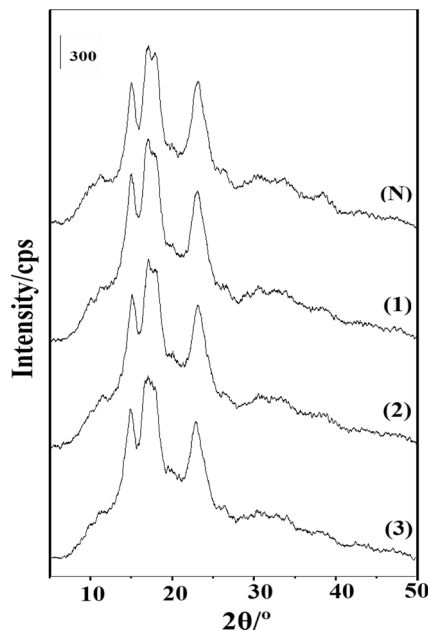
Fig. 5 Difratogram XRD: (N) native cassava starch; (1; 2; 3) native cassava starch treated with UV-light (λ=256 nm) at 1 h exposure and NaClO standard solutions 0.1; 0.2 and 0.5 mol L^{-1}, respectively

Conclusion

The double and simultaneous action of NaClO oxidation and UV light on cassava starch granules had a pronounced effect on its main properties. The TG/DTG curves of the treated samples exhibited a decrease in the thermal stability, which shifted the decomposition temperatures to lower values. The DSC curves demonstrated that the peak temperature occurred around 65–70 °C and the gelatinisation enthalpy decreased considerably between 11.01 and 5.69 J g^{-1} for the untreated and modified starches. The RVA results for seatback parameter presented starchs paste with low tendency to retrogradation to the modified samples. The average diameter of the granules was little affected but the average roughness and relative crystallinity decreased, and were inversely proportional to the

Table 4 Color parameters: (N) native cassava starch; (1; 2; 3) native cassava starch treated with UV-light (λ=256 nm) at 1 h exposure and NaClO standard solutions 0.1; 0.2 and 0.5 mol L^{-1}, respectively

Samples	L*	a*	b*
(N)	98.71±0.21[b]	−0.10±0.02[b]	1.79±0.10[a]
(1)	99.45±0.19[a]	−0.03±0.01[a]	0.82±0.13[c]
(2)	98.38±0.14[c]	−0.08±0.02[b]	1.51±0.14[b]
(3)	99.01±0.07[b]	−0.29±0.01[c]	1.64±0.10[ab]
p (Shapiro-Wilk)**	0.62	0.39	0.24
p (Brown-Forsyth)**	0.88	0.66	0.85
p (Anova)***	0.00	0.00	0.00

(**) Probability values obtained second Shapiro-Wilk test for normality and Brown-Forsythe test for homogeneity of variances, (***) Probability value obtained second analysis of variance (ANOVA), (****) Different letters in the same column represents significative difference according to Fisher LSD test ($p<0.05$)

NaClO concentration. A trend to white colour in the cassava starch was observed after the performed treatments.

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