CIENCIA en DESARROLLO

MICROWAVE AND ULTRASOUND ACTIVATION EFFECT ON CATIONIZATION OF CORN AND POTATO STARCHES

EFECTO DE LA IRRADIACIÓN ASISTIDA POR MICROONDAS Y ULTRASONIDO SOBRE LA CATIONIZACIÓN DE LOS ALMIDONES DE MAÍZ Y PAPA

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Abstract

The aim of this study was to identify and compare the effect of ultrasound (US) and microwave (MW) irradiation on the assisted synthesis reaction to obtain cationic corn and potato starch derivatives, with cationizing agent (3-chloro-2-hydroxypropyl)-trimethylammonium chloride in solution and in limited solvent conditions, known as a paste process. The starch derivatives were characterized by techniques, such as Fourier Transformed Infrared Spectroscopy, Thermo Gravimetric Analysis, Differential Scanning Calorimetry, Scanning Electron Microscopy and Atomic Force Microscopy. The application of both (MW) and (US) irradiation as energy sources

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permitted the shortening of the etherification time to minutes from the previously reported 18 hours of traditional heating. The results show the high potential of alternative energy sources to innovate and increase the efficiency of a technological starch derivatization process.

Keywords: Cationic starch, characterization, microwave, synthesis, ultrasound.

Resumen

El objetivo de este estudio fue identificar y comparar el efecto de la irradiación asistida por microondas y ultrasonido en la reacción de síntesis, para obtener derivados catiónicos a partir de los almidones de maíz y papa, con el agente cationizante cloruro de (3-cloro-2-hidroxipropil) trimetilamonio en solución y en condiciones limitadas de disolvente, conocido como un proceso en pasta. Los derivados de almidón se caracterizaron por técnicas, tales como: Espectroscopia Infrarroja de Transformadas de Fourier, Análisis Termogravimétrico, Calorimetría Diferencial de Barrido, Microscopía Electrónica de Barrido y Microscopía de Fuerza Atómica. La aplicación de irradiación por microondas y ultrasonido, como fuentes de energía, permite la disminución del tiempo de eterificación a minutos, comparado con reportes anteriores, de 18 horas de calefacción tradicional. Los resultados muestran el alto potencial de fuentes de energía alternativas para innovar y aumentar la eficiencia de un proceso tecnológico de derivatización del almidón.

Palabras clave: Almidón catiónico, caracterización, microondas, síntesis, ultrasonido.

Introduction

It has been extensively reported, that microwave (MW) heating makes reactions take place faster than under conventional thermal conditions and limit the occurrence of slower side reactions [1, 2], thus, greater yields are usually obtained. The results of the study conducted by Jyothi et al. [3, 4] indicate that succinylation of starch can be achieved in shorter reaction times, that microwave activation developed newer and versatile uses for cassava starch. Via microwave heating described a rapid method in the acetylation of cassava starch and the physicochemical properties of the obtained product [5]. Cassava starch acetylation changed starch molecular motion, resulting in a decrease in the glass transition temperature.

As published recently, zincatated potato starch was prepared in a solid-state, microwave-assisted reaction [6]. Reactions were faster than the ones proceeding on convectional heating. A series of cationic starch derivatives were synthesized by grafting a cationic moiety such as glycidyl octyl dimethylammonium chloride (GODAC), glycidyl dodecyl dimethylammonium chloride (GDDAC), and glycidyl tetradecyl dimethylammonium chloride (GTDAC), on the starch backbone, using NaOH as a catalyst [7]. During the last two decades, ultrasound microwave irradiation, became important as non-conventional forms of energy in physical and chemical processing [8], applicable as well in carbohydrate chemistry. It has been reported [9-11] that microwave and ultrasound can accelerate specific organic reactions and offer better yields.

Microwave heating involves the direct absorption of energy by functional groups that bear ionic conductivity or a dipole rotational effect, and this energy is then released into the surrounding solution [12]. This absorption of energy causes the functional groups involved to have higher reactivity to other surrounding reactants, than when simply incubated with the reactants at the same temperature. In other words, the enhanced rate of the reaction is due to the reactant being stirred by the molecular dipole rotation and the molecules themselves acting as a stirring bars. In contrast to conventional heating(CH), the salient feature of “dipole rotation” constitutes one efficient form of “molecular agitation” or “molecular stirring,” many aspects of which can be explored in chemical reactions [12]. The changes in chemical structure of ultrasound-treated cornstarch (UTCS) granules are presented and discussed in Huang, Q., et al. work [11]. After microwave assisted acetylation of starch took place, a reduction in the Tg, strong hydrophobicity, and important exo-corrosion affecting the granules were noticed. These changes were due to chemical modifications [13].

Ultrasound was used as an efficient method for microporous starch production [14, 15] and as a method of extraction. Ultrasonic irradiation offers an important potential for the conversion of biomass raw materials, such as polymeric carbohydrates, to useful lower weight molecules [8].

The use of microwave and ultrasound heating, is the focal point of this work, dedicated more specifically to the preparation of the cationic starch derivatives and simultaneously compared between the preparation in solution versus paste or cake state, with variable concentration of cationized agent and temperature. It was found that etherification could be completed during a very short reaction time under milder conditions with both types of irradiation. The obtained starch derivatives were characterized by FT-IR, TGA, DSC, SEM and AFM **Materials and Methods**

Materials

Corn and potato starches, analytical grade sodium hydroxide and hydrochloric acid were purchased from Merck-Mexico, SA, Mexico. N-(3-Chloro-2-hydroxypropyl) trimethylammonium chloride (CHPTAC) was procured from Sigma-Aldrich Co, Mexico. Quimicam S.A. of Central Valle of Mexico, supplied analytical grade isopropanol.

Microwave cationization of corn and potato starches

Different (CHPTAC) concentrations in solution

Starch was cationized by reacting samples with the cationic monomer CHPTAC, as follows: samples of 0.25 g of corn starch were dissolved in 25 ml of distilled water at 80°C for one hour and mixed with 0.360; 0.486; 0.678; 0.778 g of CHPTAC; additionally, 2.5 mL of 1 molar solution of sodium hydroxide was added to each solution [16]. Starch reactions in solution were allowed to proceed in a Discover SP CEM Microwave Synthesis System equipped with The Synergy™ software and volume independent infrared temperature sensor, which provides the simplest means to measure the reaction temperature in a non-invasive manner, for example at 50°C for 30 minutes. After that, diluted hydrochloric acid was added to lower the pH below 7 to fully stop the cationization process [17].

The reaction solutions were thereafter cooled to room temperature, and the polymer was precipitated by adding an excess of isopropanol solvent. Similar experiments were carried out under microwave assisted conditions, 0.25 g of corn starch in 25 mL of deionized water with 0.778 g of CHPTAC and 2.5 mL of NaOH 0.1 N at temperatures of 40,50,60,70,80°C.

Microwave cationization starch in cake or paste state at different temperatures

In the laboratory, native corn and potato starch samples were cationized by microwave-assisted radiation in the paste state. For this condition, 4.5g of starch was mixed with 1.218g of CHPTAC and 4.5 mL of NaOH 10 N added to the mixture. The mixture was divided into six parts; each sample reacted by microwave heating at different temperatures. The duration of the heat treatments ranged from 5 to 40 minutes. The solution was subsequently cooled to room temperature and the polymer was precipitated by adding isopropanol. It was then dried in a vacuum oven at 40°C for 4 h.

Ultrasound cationization of starch in solution

2.5 g of starch in 25 mL of water were pre-heated at 50 °C for 2 minutes using a horn-type Ultrasonic Processor Model: GEX 130 System, 20 kHz) at 70% sonic power, 130 W. Next, 0.778 g of CHPTAC and 2.5 mL of NAOH 0.1 N were added to obtained gel like solutions and the reaction was followed. Thus, sonication was applied for 5, 10, 15, 20, 25, 30 and 40 minutes, with occasional stirring, a sample was taken each time. Water cooling bath was used to maintain the temperature near 50±2°C. The products were precipitated with isopropanol and further dried at 40°C (Fig. 2a).

0.25 g of dry basis native corn starch samples were suspended in 25 mL of water, 2.5 mL NaOH 1N and mixed with 0.778 g of CHPTAC. The reaction was carried out at 40, 50, 60, 70°C using a horn-type Ultrasonic Processor Model: GEX 130 System, 20 kHz) at 70% sonic power 130 W. After that, dilute hydrochloric acid was added to each sample to lower the pH below 7 to stop the cationization process [17]. The solutions were thereafter cooled to room temperature and the polymers were precipitated adding an excess of isopropanol solvent. They were then dried in a vacuum oven at 40°C for 6 hours.

Characterization of cationic starches

Infrared Measurements

FTIR spectra of native and cationic starches were recorded on an IR Spectrum 400 Perkin Elmer FTIR Spectrometer, using the Spectroscopy Attenuated Total Reflectance (FTIR/ ATR) technique. The spectra were obtained with a resolution of 4 cm^{-1} between a wave number range of 400 and 4000 cm^{-1}. For each spectrum, 32 scans were co-added.

Thermal Analysis

Thermogravimetric Analysis (TGA). The thermal stability of the native and etherified hemicelluloses was performed using Thermogravimetric Analysis (TGA), TGA/SDTA 851e Mettler Toledo. The scans were run from 20°C to 340 °C at a rate of 10 °C per minute under nitrogen flow.

Differential scanning calorimetry (DSC). The thermal properties of selected samples were determined using a DSC 82 Mettler Toledo differential scanning calorimeter. A sample of 5 mg was weighed in a pre-weighed aluminum pan. The pan was sealed hermetically and transferred to the heating chamber of the calorimeter. An empty pan was used as a reference, and the sample was heated from -40 to 240°C at a rate of 10°C min^{-1}, and then cooled back to 20°C at the same rate. The temperatures corresponding to the onset of gelatinization (To), peak (Tp), endset (Te), and also the heat of gelatinization (ΔH) were recorded.

Scanning Electron Microscopy (SEM)

The morphology of the samples of native corn and potato starches, as well as those of the modified starches, were investigated using a LV-SEM, JSM-5600LV equipped with secondary and retro dispersive electron detectors. The instrument was set to a difference in accelerating voltage of 15 kV, operated at 12 Pa of pressure in the specimen chamber. The magnification range was changed from 100x to 1500x. SEM images were obtained with secondary electrons. For the SEM analysis, samples were fixed onto an aluminum specimen holder with carbon tape. The sample was covered with a thin layer of 500 nm of carbon, especially if the sample was a poor conductor, to prevent electric charge on the surface of the sample.

Atomic Force Microscopy (AFM)

AFM imaging was carried out using a MAF JSPM-4210 Scanning Probe Microscopy Instrument (JEOL) in air at ambient temperature and humidity controlled. Starch and cationic derivatives samples were spread directly on an AFM sample holder. The images of native and cationized starches were recorded in the tapping mode. The topographic and amplitude images were taken simultaneously. Silicon probes were used with a nominal spring constant of 20–100 N/m and a scan frequency of 0.5 Hz. Scan areas were of 2x2 μm, 3x3 μm, 4x4 μm.

Results and Discussion

Microwave and Ultrasound

Table-1 shows the effect of temperature and time on conversion, for a constant amount of starch sample of 28×10^{-3} mol or 28 mmol and 46 mmol of CHPTAC with 45 mmol NaOH. The results show reactions assisted by MW, experiments done in paste state, time and temperature increases the conversion percentage. Corn samples at 60 ° C and 10 min the conversion was reduced. At 70 °C and 5 min the conversion is maximal.

Sample	Corn starch Temperature °C	Corn starch Time (minutes)	Corn starch Conversion %	Potato starch Temperature °C	Potato Starch Time (minutes)	Potato starch Conversion %
1	50	5	42	60 nfrmemneafdbvc	5	70
2	55	5	62	65	5	82
3	55	10	88	70	5	84
4	60	5	91	60	10	91
5	60	10	77	65	10	92
6	70	5	97	70	10	96

Table 1. Synthetic details of corn and potato cationic starch derivatives, by microwave irradiation (p)

Figure (1) shows the percentage conversion versus the CHPTAC molar concentration data for corn and potato starch samples. Both reactions were activated by microwave at a constant temperature of 50°C in solution. Figure (1) shows that, as expected, increasing CHPTAC monomer concentration, the conversion percentage of polymer modification increased for both samples corn and potato in solution reaction assisted by microwave irradiation, and better yields were observed for corn samples.

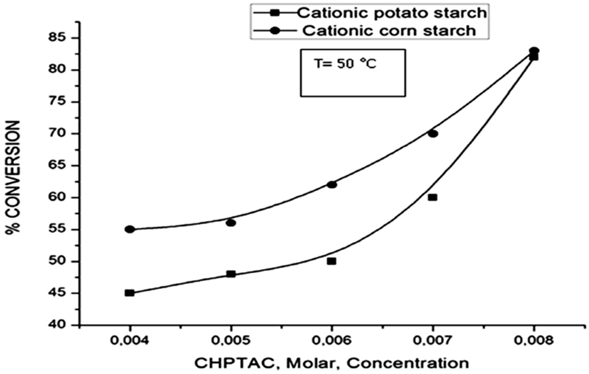

Figure 1. Concentration of CHPTAC, versus percentage conversion of Cationic Starches by MW irradiation

The application of ultrasound irradiation as an energy source, shortened the etherification time to several minutes and increased the efficiency of starch cationization. From Figure 2a, a better conversion was observed for ten to twenty minutes at the same temperature.

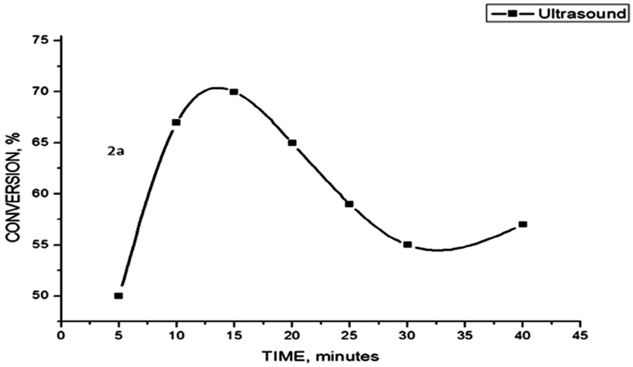

Figure 2a. Conversion of cationic corn starch in solution by ultrasound.

Figure 2b shows experimental conditions and results for two cationic starches. The first reaction for corn starch sample was assisted by microwave irradiation; the second reaction for potato starch was activated by ultrasound. The samples assisted by ultrasound activation reached a maximum of percentage conversion at 50°C. The other sample obtained by MW irradiation attained a maximum percentage conversion at 70°C. As it can be perceived, the ultrasound activated reaction proceeded well at low temperatures, which is a promising so the technique can be applied successfully with significant energy savings. Figure 2b shows a coincidental time conversion, while at higher temperatures there is a decrease in polymer modification.

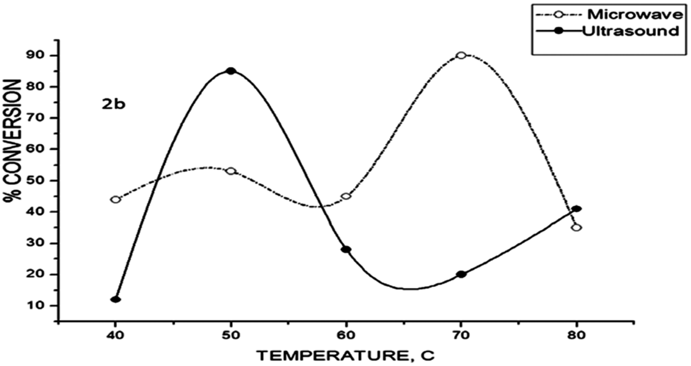

Figure 2b. Conversion of cationic corn starch by microwave and cationic potato starch in solution by ultrasound.

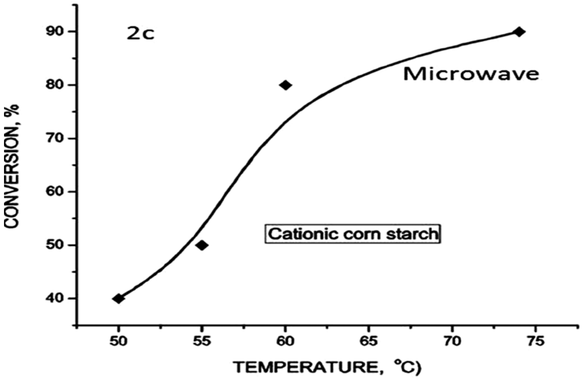

Figure 2c. Conversion of cationic corn starch by microwave related to temperature.

Ultrasound activation is a unique phenomenon of cavitation, generates high-energy and/or excited state species, thereby inducing a cascade of radical and electron transfer (ET) processes with subsequent bond breaking of compounds present in the solution. The extreme local conditions provided by the cavitational collapse, occur during extremely short times, a few microseconds, which ensures an almost adiabatic process [18]. In our case, the dispersive effect is important because starch particles disperse out and react quickly and effectively with the CHPTA agent at higher temperatures.

Figure 2c shows the percentage conversion of corn starch at different temperatures. For example, 0.0040 molar of starch reacted with a controlled amount of cationizing agent 0.0080 molar of under identical conditions as previously described synthesis under microwave irradiation. This synthetic pathway is more efficient at higher temperatures in a temperature range studied of 60 to 70°C. The MW and US irradiation led to shorter reaction times and was dependent upon the dipole strength of reactants, its mobility and mass and the matrix state of the dipole [19].

The experiments showed the influence on the cationic efficiency of various factors. For the same concentration of cationic agent and raw starch, the effects of reaction time, temperature, and phase state of the medium were investigated. The products exhibited the better percentage yield in a temperature range of 60–70°C with ten minutes reaction time and were consistent with previous studies [20-22].

Figure 2d indicates the influence of temperature and time on the process of cationization of potato starch in a paste state. It can be seen that time extended to 10 minutes favors the cationization process in the range of temperatures studied. If the microwave irradiation is maintained for five minutes, the best temperature for high conversion is 65°C.

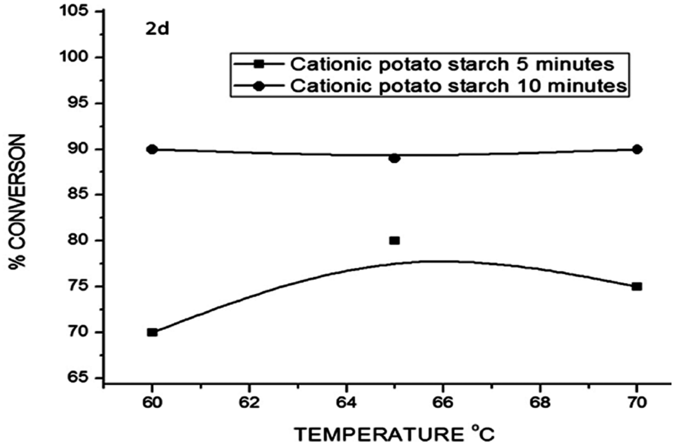

Figure 2d. Conversion of cationic potato starches by microwave irradiation.

The cationic potato starch derivative will have the highest yield of the reaction at a temperature of 60°C, if microwave irradiation is hold up for ten minutes. Not important difference in percentage conversion was observed, when this reaction was run at temperatures higher than 60°C, even if it reaches 70°C. Effective starch modification can be achieved when microwave irradiation supports the activity of the cationizing agent added to the reaction mixture.

Infrared Spectra

The FTIR spectra of potato starch and the cationic potato starch derivative are shown in Figure 3. For the potato starch, in (Figure 3), the broad peak at 3351.34 cm^{-1} is due to the H_2O stretching vibration. The two bands at, 2924.43 cm^{-1} are due to antisymmetric and symmetric stretch respectively, and 1151 cm^{-1} are due to the C–O stretching vibration. The peak at 1639.87, cm^{-1} is due to the first overtone of O–H bending or H_2O deformation. Two bands at 1077 and 1022 cm^{-1} are for the CH_2–O–CH_2 stretching vibration.

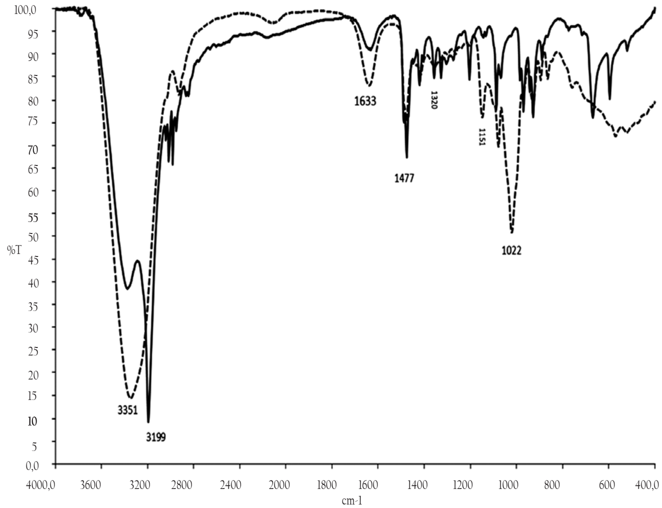

Figure 3. FTIR Spectra: Infrared Spectrum of potato starch.
__ Infrared Spectrum of cationic potato starch, microwave assisted.

For the cationic potato starch, (Figure 3), the broad peak at 3320cm^{-1} is due to the H_2O stretching vibration. The two bands at, 2924.43cm^{-1} are due to antisymmetric and symmetric stretch respectively, and 1149.5 cm^{-1} are due to the C–O stretching vibration. The peak at 1644cm^{-1} is due to the first overtone of O–H bending or H_2O deformation. The band at 1320 cm^{-1} is due to CH_2, CH deformation. The bands at 1000 cm-1 are due C-OH stretch vibration, and the band at 840cm^{-1} CH_2–O–CH_2 correspond at ring mode stretching vibration [23].

The presence of an additional band at 1405 cm^{-1} assignable to the C–N stretching vibration, which is not present in raw starches, is clear proof of the incorporation of a cationic moiety onto the backbone of the starch. It should be mentioned that such a band was absent in starch. It is worth mentioning, the band corresponding to C–Cl at 671cm^{-1} was absent in the cationic product. According to the literature and to the reference spectra, the fundamental stretching and deformation vibrations of the CH3 groups in trimethylammonium $(CH_3)_3N_1$ are expected at approximately 3100-3020 cm^{-1} and 1477 cm^{-1} [23] .

Thermogravimetric Analysis (TGA)

Figures 4.1 and 4.2 show the mass loss of four starch samples recorded by (TGA) analysis and the correspondent DTG curves. Figure 4.1 cationic corn sample prepared by microwave activation in paste state. The TG and DTG curves, and thermo-grams of native and cationic starches: cationic corn in paste by microwave (mw) irradiation (Fig. 4.1.1); cationic potato in paste (mw) (Fig. 4, 1, 2); cationic corn (mw) in solution (Fig. 4.1.3); and cationic potato (mw) in solution (Fig. 4.1.4). These samples are compared with a raw starch (Fig. 4.1.5). From the TG curves displayed in Fig. 4.1 we observe that on further increase in temperature there was a sharp mass loss at 313°C for native cornstarch (Fig. 4.1.5), at 242°C for cationic corn (mw) in solution (Fig. 4.1.3), and at 259°C for cationic cornstarch microwave in paste (Fig. 4.1.1). All mass losses resulted from the partial decomposition of cationized starch. From Fig. 4.1 we can identify differences between the samples, and the thermal stability and degradability of starch derivatives can be noted as well. Thermograms for cationic corn and potato starches, microwave assisted in solution; degrade in a similar manner (Fig. 4.1.3 and Fig. 4.1.4).

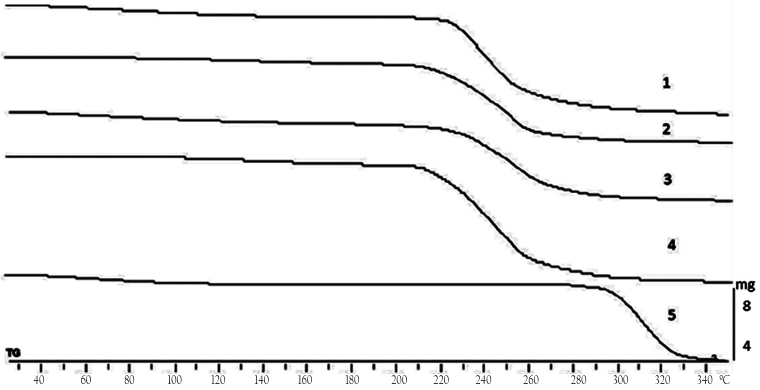

Figure 4.1. TGs: Cationic starch samples prepared by microwave activation: 1.Corn paste. 2. Potato paste 3. Corn in solution. 4. Potato in solution. 5. Raw starch.

Cationic corn and potato derivatives obtained by microwave in a paste state behave different in Figures 4.1.1 and 4.1.2. The first degradation stage occurs for both within the interval of 128-140°C and the second strong weight loss within the interval of 230-248°C, showing the increase of thermal stability of the starches prepared in a paste state over those obtained in solution and completely microwave assisted. The chemically modified starch samples lose mass earlier than the original corn sample.

The DTG curve obtained for cationic corn starch microwave (mw) in paste, is illustrated in Fig. 4.2a, cationic potato (mw) in solution in Fig. 4.2b, native cornstarch in Fig. 4.2c, and cationic corn (mw) in solution in Fig. 4.2d. From the graphs in Fig. 4.2c, we can see that they are samples in which there was a mass loss of 9% around the gelification point temperature of 67-68°C for cornstarch, and the correspondent cationized Fig 4.2a does not present mass loss. From the DTG plot Fig. 4.2c, it can be observed that the thermal degradation of native starch commenced at 288°C following a significant mass loss with an increase in the temperature to 318°C. However, the cationic starch was thermally decomposed at a temperature of 233°C, and the rate of mass loss was rapid between 240 and 265°C, which were low temperatures in comparison to the native starch. Clearly, the cationically modified starches undergo thermal degradation at a lower temperature than in the case of native starch. This indicates that the thermal stability of cationic starch decreased due to the cationization. This result was similar to those described by [24] and [25], who examined the effect of chemical modification on starch by using the thermal analysis method.

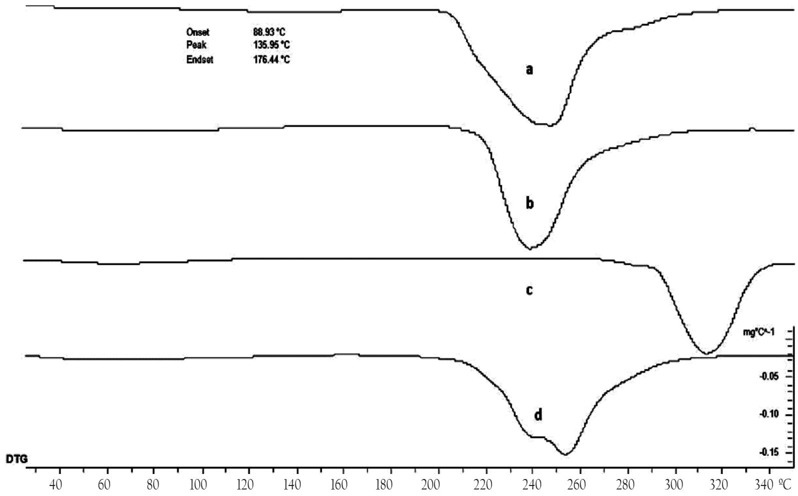

Figure 4.2. DTGs: (a) Cationic corn (mw) paste. (b) Cationic potato (mw) in solution. (c) Corn starch. (d) Cationic corn (mw) in solution.

Cationic potato obtained by microwave in solution degrades in two stages. The first stage begins at about 82.6°C for all the material with a weight loss of 6.3 % this is due to loss of residual water. The second stage exhibited a rapid weight loss at 220°C reaching its maximum at 240°C as shown in Fig. 4.2b. Cationic corn obtained in solution by MW activation its first weight loss of 8.54%. at 58.99°C. The second peak reached its maximum at 257°C.

Differential Scanning Calorimetry (DSC)

Differential Scanning Calorimetry (DSC) has become widely accepted as the most suitable method for the evaluation of different carbohydrate gelatinization, starch gelatinization as a multistage process [26], and other thermal behavior [27-30]. DSC thermo-grams facilitate the analysis of starch transition temperatures (i.e. onset, T_o; peak, T_p; and conclusion, T_c) [31]. The thermal behaviors of our samples are shown in Fig. 5: cornstarch Fig. 5a, cationic corn microwave (mw) in solution Fig. 5b, cationic potato starch in paste Fig. 5c, cationic corn starch (mw) paste Fig. 5d, and cationic potato starch (mw) in solution Fig. 5e. DSC of native corn Fig. 5a gelatinizes in a temperature range between 78 and 94°C before retro-gradation sets in. Modified starches extending the retro-degradation temperature heavily show

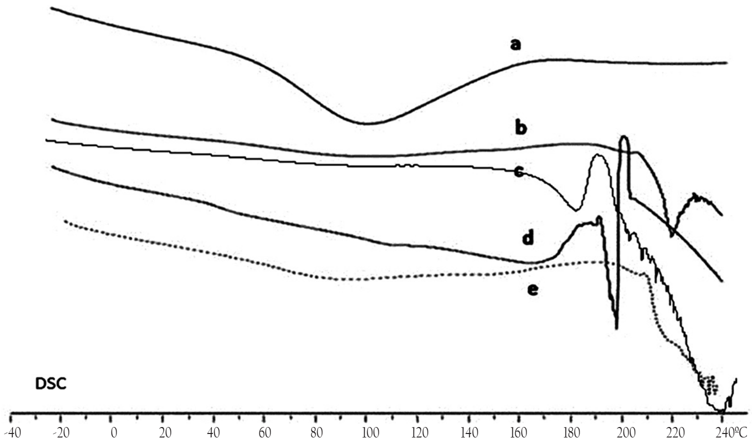

Figure 5. DSCs behavior of raw starch and its corresponding cationic derivatives: (a) Corn starch. (b) Cationic corn (mw) in solution. (c) Cationic potato starch (mw) in paste. (d) Cationic cornstarch (mw) in paste. (e) Cationic potato starch (mw) in solution.

a decrease in the stability of the cationic product [32, 33]. The calorimetric data in Fig. 5 clearly shows the difference among the starch derivatives. For example, corn starch containing water (Fig. 5a) was submitted to thermal processing with temperatures above 100ºC. This activity shows the gelatinization process of the starch in such a way that it melts and presents only a one phase transition attributed to water vaporization [3

The single narrow endotherm for cationic corn microwave in solution Fig. 5b, and cationic potato starch microwave irradiated in solution Fig. 5e, related to the water-mediated melting of starch crystallites, were initiated by the stripping of starch chains in the swollen amorphous regions [35]. For cationic potato starch microwave in a paste state (Fig. 5c) and for cationic corn starch in the paste state Fig.5d, the endothermic heat flow that was found in the DSC tests was low. This finding was probably due to overall gelatinization during the reaction condition and the drying process before the DSC test.

A close analysis of the DSC endotherms shows important differences in the thermal behavior of these samples. There is some similitude between starches and corresponding derivatives in solution as deduced from the curves shown in Fig. 5. For example: for corn starch (Fig. 5a), To 22, 49; Tp corresponded to 94.01°C and Te equaled 167.62°C for cationic corn microwave in solution (Fig. 5b), Tp 74, 40 and Te 181, 62°C; for cationic potato (mw) in solution, Tp is 87.38°C. There is a peak displacement for cationic derivatives in a paste state as we can see from the same graph example: To 4.33; Tp equal 163.98°C and Te 185.95 °C for cationic corn (mw) in paste (Fig. 5d) or similar in cationic potato starch (mw) paste Fig. 5c, where Tp is 182.35°C. Analysis of DSC endotherm has established the water dependency of starch gelatinization. Tp becomes higher for microwave irradiated starches in paste and indicated a stronger or irregular arrangement of molecules after cationization. The decrease of water content in cationic starch derivatives produced structure changes and led to the increase of the glass transition temperature, which could indicate better molecular order within the granule after substitution. Several researchers revealed that chemical substitution served to facilitate the melting of amylopectin crystallites [29, 36].

Scanning Electron Microscopy (SEM)

The images obtained by SEM of potato and corn starches and the respective modified starches by cationization are shown in Figs. 6.1 and 6.2: SEM images of native corn starch Fig. 6.1a, native potato starch Fig.6.1b, and their corresponding cationized derivatives Fig. 6.1c, and Fig.6.1d. Samples of the cationic starch derivatives correspond to cationic potato and corn starches obtained by microwave radiation in paste at 60 or 70°C for 10 minutes.

The changes in the structure of ultrasound-treated corn starch granules are presented and discussed. We found that the Scanning Electron Microscopy (SEM) of the crystalline structure of treated granules did not change, but the amorphous area was slightly destroyed [11].

Figure 6.1 shows the scanning electron micrographs of the native and cationic starches. Native cornstarch Fig. 6.1a presents granules with irregular shapes and various sizes. The surface morphology of potato starch, Fig 6.1b, is more regular; the granules are generally large, voluminous, and oval-shaped with an eccentric hilum. When viewed under polarized light, the granules are birefringent, indicating a high degree of molecular order within the granule. Modified starches (Fig. 6.1c and Fig. 6.1d) are not similar to native cornstarch, as more evident planar configuration was observed on some granular surface. Some inward concaves were also found in the granules of Fig. 6.1c, along with partially disintegrated granules and small fragments. SEM photos showed that the paste process deformed the starch granules.

Fig. 6.2 shows SEM images of potato cationized starch derivative Fig. 6.2a, Fig. 6.2b, Fig. 6.2c, and Fig.6.2d sequentially with their deformation influenced by exposure to electrons. The granules of Fig. 6.2 displayed the highest extent of fragmentation. Some large granules have especially deep holes that form pores at their surface Fig. 6.2.d. The inward concaves on the surface of the starch was also reported in reference [35] on starch citrates. The cause of the inward concaves might be a result of the swelling of starch granules during the cationization process, followed by a collapse during cooling after the termination of the reaction. The collapsed region is believed to be less organized than the rest of the granule and is the region where cationization mainly occurred. The increased superficial porosity might facilitate the diffusion of the cationizing agent into the inner region and contribute to the alteration of granular morphology. Fig. 6.2a shows a clear appreciation of rapid sequential deformation just during the photography. Through Fig.6.2.d it is evident that the sample's exposure to the electrons' beam energy during the test is an aspect that requires further studies.

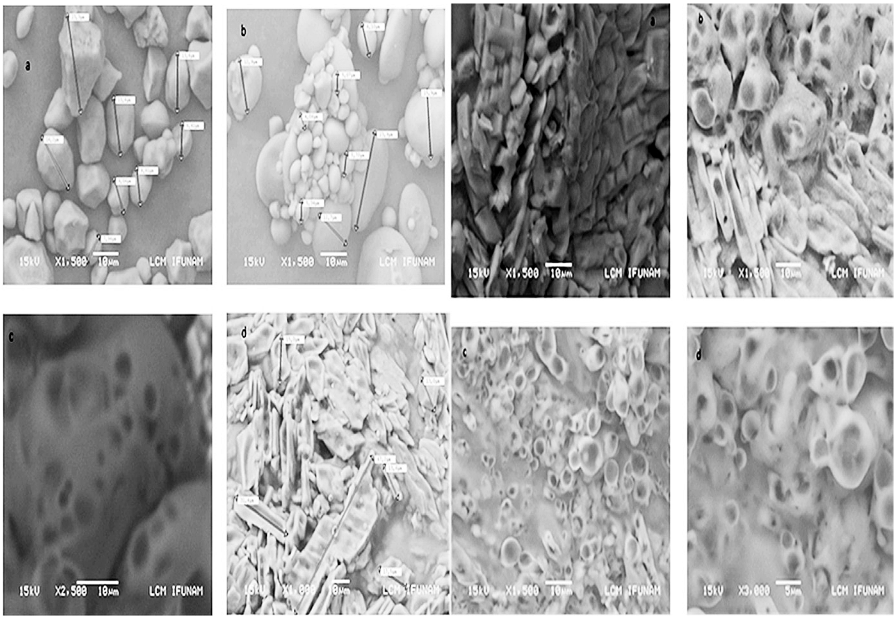

Figure 6. Fig. 6.1 SEM images of native corn (a), potato (b) starch granules and their corresponding cationized derivatives (c) and (d). Fig.6.2 SEM sequentially images of cationic potato starch derivative (a), (b), (c), (d) and their deformation influenced by exposition to electrons.

Atomic Force Microscopy (AFM)

Fig.7.1 shows changes of corn starch (Fig. 7.1a), potato starches (Fig. 7.1b), and their respective cationic corn (Fig, 7.1c) and cationic potato (Fig. 7.1d), with rough surfaces qualitatively characterized by AFM. This investigation showed that native potato and cornstarch granules, similar to cationic derivatives, have very complex surfaces consisting of numerous fine particles with diameters of 20–40 nm. In general, starch cationized derivatives have a large-scale coarse surface with a ridge-and-valley structure with many depressions. α-amylase action caused the shortening of carbohydrate chains and the extension of surface roughness Fig. 7.1 [37].

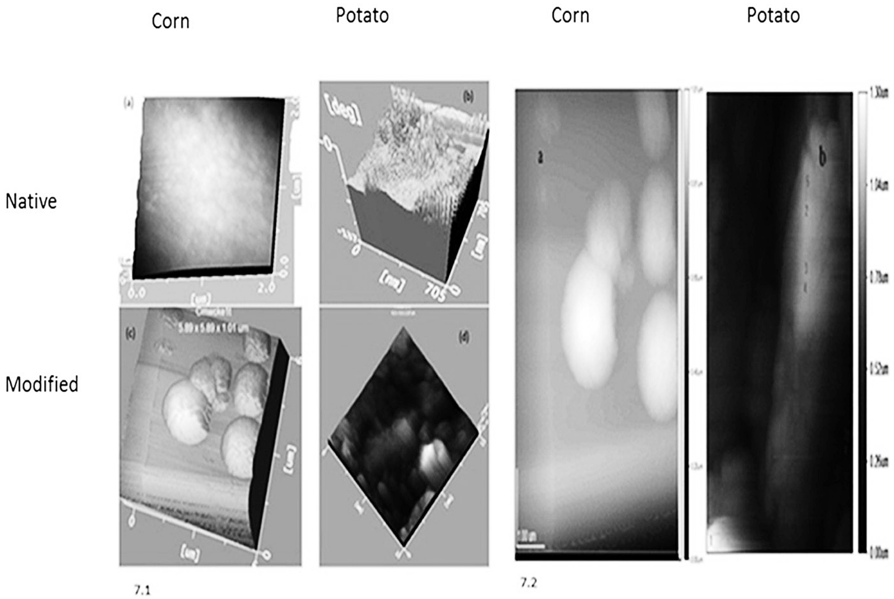

Figure 7.1. Changes of corn (a) and potato (b) starches and their respective cationized (c), (d) roughness surface qualitatively characterized by AFM. Fig.7.2 AFM images taken in tapping mode of derivative surfaces of cornstarch in solution and cationic potato derivative in paste stage, assisted microwave irradiation. The image surface area is 1μm x 1μm (a) and 1μm x 1.3μm (b).

In the following Fig.7.2, we can see AFM images taken in tapping mode of derivative surfaces of cationic cornstarch in solution (Fig. 7.2a) and cationic potato derivative in paste (Fig. 7.2b), assisted by microwave irradiation. The image surface area is 1μm x 1μm (a) and 1μm x 1.3μm (b). The layered structure of the cationic corn and potato starch granules in paste and the surface revealed by AFM offers the advantage of highly localized (~nm) topographic imaging, into granular structure. Fig. 7.2a and Fig. 7.2b show the 3D topographical view of corn and potato starch in paste state. The raw starch exhibits a smooth topography, it clearly shows that the surface of the starch is composed of larger blocklets of size ranging from 100 to 200 nm separated by gaps. Each blocklet is further composed of smaller blocklets 20–30 nm in size separated by much shallower depressions and a potato modified rough surface starch due to the presence of modified components present in the polymer.

Conclusions

The results unequivocally confirmed the highly positive effect of ultrasound and microwave irradiation-assisted reactions of starch cationization with CHPTAC, as comparable percentage conversions, were achieved within five to ten minutes under related reaction conditions, for incorporating a cationic moiety onto the backbone of polysaccharide. For corn and potato starches in a paste state, by microwave and ultrasound irradiation, might produce cationized derivatives with higher levels of substitution. In the solution for corn derivatives, modification occurs during very short reaction times, and DSC offers evidence for better transformations in cationic cornstarch in solution and paste. TGA results show that cationic starches lose thermal stability with regard to raw material. These results also confirm the presence of the modified material distinct from the native one due to the occurrence of the double peaks in the cake state process for both corn and potato derivatives. SEM and AFM observations confirm findings for the surface structure. Pronounced modification of granular potato starch morphology was obtained after the cationization process.

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