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Surface Modification of Cellulose from Oat Hull with Citric Acid Using Ultrasonication and Reactive Extrusion Assisted Processes

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Abstract: This study aimed to produce modified cellulose extracted from oat hulls by an esterification reaction with citric acid (CA) employing ultrasonication and reactive extrusion assisted processes. Modified samples were characterized by Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (DRX), scanning electron microscopy (SEM), wettability, oil and water absorption capacities, water adsorption capacity, and thermal stability. From FTIR results it can be observed a new band for all modified samples at 1735 cm^{-1} , confirming the esterification. The morphology and crystallinity pattern of fibers were not affected by esterification, and crystallinity indexes ranged from 43% (unmodified cellulose) to 44–49% in modified samples. Both groups of samples, obtained by ultrasonication and reactive extrusion, showed decreases in water absorption capacities (1.63–1.71 g/g) compared to unmodified cellulose (9.38 g/g). It was observed an increase in oil retention capacity from 1.80 g/g (unmodified cellulose) to 4.57–7.31 g/g after esterification, and also the modified samples presented higher affinity by a non-polar solvent in the wettability test. The new properties of modified cellulose expand its use in the industry and prove that ultrasonication and reactive extrusion can be used to obtain esterified cellulose, being eco-friendly, simple, and convenient processes with short reaction times.

Keywords: lignocellulosic residue; hydrophobicity; organic acid; esterification



Citation: Gil Giraldo, G.A.; Mantovan, J.; Marim, B.M.; Kishima, J.O.F.; Mali, S. Surface Modification of Cellulose from Oat Hull with Citric Acid Using Ultrasonication and Reactive Extrusion Assisted Processes. *Polysaccharides* **2021**, *2*, 218–233. <https://doi.org/10.3390/polysaccharides2020015>

Academic Editor: Hyun Chan Kim

Received: 18 February 2021

Accepted: 23 March 2021

Published: 1 April 2021

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1. Introduction

The transformation of agroindustrial residues into new bio-based materials, maximizing the utilization of lignocellulosic biomass and minimizing the waste generation, encompasses the biorefinery concept. This is also according to the main premise of a circular economy, which supports the concept of industrial synergy that is encouraged by the reuse of residues within the industrial network, acting as a mechanism for a sustainable future [1].

Additionally, materials obtained through renewable resources have been developed in the last decades as alternatives to replace fossil resources, being able to be redirected to the development of green technologies through biotechnology to obtain products with high added value, minimizing the dependence on fossil-based resources and reducing the generation of solid and liquid wastes [2–4].

The use of lignocellulosic residues such as wheat straw, rice hulls, soybean hulls, orange bagasse, corn hulls, corn fiber, and oat hulls to obtain cellulose can be an interesting alternative to valorize these materials, which generally contain about 20–50% cellulose, 20–30% hemicellulose and 20–30% lignin, offering great opportunities for sustainable production integrated with biorefinery processes to obtain bio-based materials [1,5–8].

Considering their global availability, there is great interest in the conversion of lignocellulosic biomass into the derivative products of cellulose [9]. Cellulose has remarkable

characteristics such as tensile strength, elasticity, durability, and in addition to high water absorption and retention capacity, and biodegradability, it is neither toxic nor allergenic; because of these properties it is considered a high potential bio-based material, with versatile applications in wastewater treatment [10], packaging [11,12], food industries [13–15], drug delivery systems [16], and tissue engineering [17].

Regardless of its origin, it is a naturally occurring semicrystalline linear homopolymer composed of D-glucose units linked by β -(1→4)-glycosidic bonds, presenting crystalline and amorphous regions, containing three hydroxyl groups per glucose unit that can participate in several reactions, which makes cellulose a versatile platform for surface chemical modifications [18–20].

The introduction of an ester group to the cellulose skeleton through the reaction of esterification of hydroxyl groups provides a hydrophobic character to cellulose, making it more compatible with non-polar polymers and solvents [20–23].

The use of carboxylic acids to modify cellulose is less aggressive to the environment, such as citric acid (CA), which appears as a low cost and sustainable esterification agent capable to change the hygroscopic character through a direct chemical modification to increase hydrophobicity of cellulose or nanocellulose. Further, as stressed by several authors, it is an esterification agent able to overcome toxicity and costs associated with other esterification agents [21,24–30]. Several authors also reported the use of anhydrides as esterification agents, such as succinic, acetic, butyric, and hexanoic anhydrides [31,32].

CA is a tricarboxylic acid and its reaction with cellulose occurs due to the attachment of the carboxylic group via esterification with a cellulosic hydroxyl group, and also a further reaction via esterification with another cellulosic hydroxyl group can produce a crosslink between cellulose chains [25], resulting in cellulose with increased hydrophobicity.

According to Wang et al. [20] and Kostag et al. [23], carboxylic acids have low reactivity and it is necessary the use of activating agents that can break hydrogen bonds in cellulose supramolecular structure, and some of them present high toxicity or result in cellulose degrading side reactions. The use of combined chemical and physical processes can overcome the low reactivity of carboxylic acids. In this study, two different physical processes were employed to obtain cellulose esterified with CA, ultrasonication and reactive extrusion, since these both methods can act favoring the disruption of the inter- and intramolecular hydrogen bonds and subsequently allowing esterification to occur [33,34].

There are few studies in the literature exploring the use of ultrasonication or reactive extrusion assisted processes to obtain modified cellulose. Bhandari et al. [35] obtained carboxymethyl cellulose by reactive extrusion emphasizing that is a process with a short reaction time. Zhang et al. [33] reported the chemical modification of cellulose by reactive extrusion in ionic liquid; they stressed that reactive extrusion can destroy the regularity of cellulose chains and the hydrogen bond network efficiently, favoring chemical modifications of cellulose. Udoetok et al. [34] obtained crosslinked cellulose-epichlorohydrin and Tang et al. [36] obtained esterified nanocellulose, both using ultrasonication assisted processes; they stressed that when ultrasonication was used, the extent of modification was improved by the loss of the cellulose fibril structure, which was attributed to the acoustic cavitation effects of ultrasonication.

Reactive extrusion is considered an eco-friendly technique that can be used for chemical modification of polymers [7,33,35,37,38] since no solvent was involved during the process. Ultrasonication also can be considered a simple and convenient method for surface modification of cellulose [33,36], and in this study no toxic solvent was employed.

The objective of this work was to produce modified cellulose extracted from oat hulls by an esterification reaction with CA employing ultrasonication or reactive extrusion assisted processes. Modified cellulose samples were characterized by Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), scanning electron microscopy (SEM), wettability, oil and water absorption capacities, water adsorption capacity, and thermal stability.

2. Materials and Methods

2.1. Materials

The oat hull sample used in this study was supplied by a local oat processing industry (SL Cereais e Alimentos, Paraná, Brazil) Citric acid (CA) (Sigma-Aldrich, Darmstadt, Germany) and all reagents used in this study have analytical grade (PA).

2.2. Extraction of Cellulose from Oat Hulls

Approximately 50 g of oat hulls were dispersed in 500 mL of peracetic acid solution (50% acetic acid, 38% hydrogen peroxide, and 12% distilled water) at 60 °C with stirring for 24 h. After this treatment, the sample was washed with distilled water until pH 5.5–6.5 was achieved, and then it was dried at 35 °C until constant weight.

The cellulose and hemicellulose contents of the raw and bleached oat hulls were determined by the Van Soest method [39] and the lignin content was determined according to a standard method of the Technical Association of Pulp and Paper Industry [40].

2.3. Surface Modification of Cellulose

Two processes were employed to surface modification of cellulose with CA, ultrasonication and reactive extrusion.

Ultrasonication was performed according to the modified protocol described by Dong et al. [41], where 2.5 g of cellulose was dispersed in 38 g of ethanol, with the addition of 40% CA (g acid/100 g cellulose) with continuous stirring. Each mixture was submitted to ultrasound apparatus (Fisher Scientific Sonicator model 505, Pittsburgh, PA, USA), coupled with a probe with a tip diameter of 1.27 cm (Fisher Scientific model FB 4219, Pittsburgh, PA, USA), employing the following operational conditions: 40% amplitude for 1 or 2 min (samples labeled as US401minCA and US402minCA) and 80% amplitude for 1 or 2 min (samples labeled as US801minCA and US802minCA). The samples were taken to the oven (Tecnal, São Paulo, Brazil) at 110 °C for 2 h and the material was washed with ethanol by centrifugation (Hettich centrifuge, universal model 320R, Darmstadt, Germany) for 30 min at 9000 rpm three times and dried at room temperature. Samples were ground to produce particles ranging from 150 to 220 µm.

Reactive extrusion was performed in a single-screw extruder (AX Plastics, Diadema, SP, Brazil) with a diameter of 1.6 cm and a length/diameter ratio of the screw (L/D) of 40 was used, with four heating zones at 120 °C and a matrix 0.8 cm diameter with 50 rpm screw speed. Two different treatments were performed: (1) cellulose control sample was extruded without any reagent other than water, which resulted in a final moisture content of 32% (sample labeled as ECW); and (2) cellulose extruded with 40% of CA (g acid/100 g cellulose) (sample labeled as EMCCA). CA acid was dissolved in distilled water and mixed with cellulose for 10 min in a sealed plastic bag with constant manual stirring, obtaining a total mass of 100 g to be extruded, resulting in a final moisture content of 32%. The obtained extruded samples were washed three times in a centrifuge using ethanol, dried at room temperature, and milled to obtain particles ranging from 150 to 220 µm.

2.4. Characterization of Modified Cellulose

2.4.1. Fourier Transform Infrared (FTIR) Spectroscopy

Dried samples were incorporated into potassium bromide and subjected to high pressure for the production of tablets. Infrared spectra were recorded on a Shimadzu FTIR Prestige-spectrometer (Japan) in the range of 4000–500 cm⁻¹, which has a spectral resolution of 4 cm⁻¹.

Esterification extension between CA modified samples was compared from the ratio between the absorption intensity of the ester carbonyl (C=O) stretching vibrations band at 1735 cm⁻¹ (A₁₇₃₅) and the absorbance intensity of the aliphatic C–H stretching vibration at 2929 cm⁻¹ (A₂₉₂₉), which was used as an internal standard because it remained unchanged after the esterification reactions [42].

2.4.2. X-ray Diffraction (XRD)

XRD was performed using Panalytical X'PERT PRO MPD diffractometer (Almelo, The Netherlands) with copper K α radiation ($\lambda = 1.5418 \text{ \AA}$) under 40 kV and 30 mA operating conditions. Scanning ranged from $2\theta = 2$ to $2\theta = 50^\circ$, step -0.1° and speed $1^\circ/\text{min}$, equipped with a secondary graphite beam monochromator. The crystallinity index (CI) was calculated by the method of Segal et al. [43], where $CI = ((I_{002} - I_{am}) \times 100)/(I_{002})$; where, CI is the crystallinity index of the cellulose, I_{002} the peak intensity (002) ($2\theta = 20\text{--}22^\circ$), and I_{am} is the peak intensity corresponding to the peak at $2\theta = 18^\circ$.

2.4.3. Thermogravimetric Analysis (TGA)

TGA of the samples were performed using the Shimadzu TGA-50 (Japan) equipment. The scans were performed at room temperature up to 600°C with a heating rate of $20^\circ\text{C}/\text{min}$ under a nitrogen flow of $20 \text{ mL}/\text{min}$.

2.4.4. Differential Scanning Calorimetry (DSC)

DSC analysis were performed on a Shimadzu DSC 60 calorimeter (Kyoto, Japan). Samples were placed in aluminum containers and heated from room temperature to 400°C , with a heating rate of $20^\circ\text{C}/\text{min}$ in a $50 \text{ mL}/\text{min}$ nitrogen atmosphere.

2.4.5. Scanning Electron Microscopy (SEM)

SEM analysis were performed on the FEI Quanta 200 equipment (OR, USA). Samples were incubated in an air circulation oven (Marconi MA 035, Piracicaba, Brazil) at 60°C for 3 h and then kept in desiccators containing anhydrous calcium chloride for one week. The dry samples were assembled for viewing on bronze stumps using double-sided tape. Afterward, the samples were covered with a thin layer of gold (40–50 nm) and an accelerated voltage of 20 kV was used for all samples.

2.4.6. Wettability

Samples were mixed in two immiscible solvents with different densities, water ($d: 1.000 \text{ g cm}^{-3}$) and dichloromethane ($d: 1.335 \text{ g cm}^{-3}$), thus allowing to observe the affinity of the samples for each substance [44].

2.4.7. Water Absorption Capacity (WAC) and Oil Absorption Capacity (OAC)

WAC and OAC of samples were determined according to the modified methodology described by Lu et al. [45]. Approximately 0.05 g of each sample (M_0) and 1.5 mL of water (or soybean oil) (M_1) were added to a previously weighed centrifuge tube. The samples were kept in a water bath for 30 min and then centrifuged for 30 min at 9000 rpm (Hettich Centrifuge, Universal model 320R, Darmstadt, Germany). The non-adsorbed water (or soybean oil) (M_2) was removed and the water (or soybean oil) absorbed by the samples was estimated as the difference between M_1 and M_2 . WAC was calculated as: $WAC (\text{g}/\text{g}) = (M_1 - M_2)/M_0$ and OAC was calculated as: $OAC (\text{g}/\text{g}) = (M_1 - M_2)/M_0$.

2.4.8. Moisture Sorption Isotherms

Samples (0.25 g) were pre-dried for 24 h in a ventilated oven at 50°C (035 Marconi MA, Piracicaba, Brazil), and then the samples were placed at 25°C in desiccators containing different saturated solutions of salts providing specific relative humidity (RH) (11%, 38%, 46%, 60%, 75%, and 90% RH [46]). The equilibrium moisture content of each sample was calculated as the increase in dry mass of the sample for each RH condition after 7 d, and it was determined in a ventilated oven (035 Marconi MA, Piracicaba, Brazil) by drying at 105°C .

Equilibrium moisture content of each sample was plotted as a function of water activity (a_w) ($\text{RH}/100$), and the experimental data were fitted according to the Guggenheim-Anderson-de-Boer (GAB) model [47], determined by non-linear regression using the Statistica software 7.0 (Statsoft, Oklahoma, EUA). The isotherm model of GAB can be expressed

as follows: $M = m_0CKa_w / (1 - Ka_w) (1 - Ka_w + CKa_w)$, where M is the moisture content of the equilibrium in a given water activity (a_w), m_0 is the monolayer value (g water/100 g solids), and C and K are GAB constants. All tests were performed in triplicate.

2.5. Statistical Analysis

The Statistica software version 7.0 (Statsoft, Tulsa, OK, USA) was employed to perform the Tukey's test for comparing means ($p \leq 0.05$).

3. Results

3.1. Cellulose Extraction

The non-cellulosic fraction present in the oat hull was removed by the bleaching process using peracetic acid, resulting in a cellulose rich material. While raw oat hull had 26% cellulose, 30% hemicellulose, and 21% lignin; the bleached material presented 83% cellulose, 7% hemicellulose, and 3% lignin. The process yield was 33%, each 100 g of raw oat hull resulted in 33 g of this bleached material.

3.2. Fourier Transform Infrared (FTIR) Spectroscopy

FTIR spectra of all samples are presented in Figure 1, and they were used to identify functional groups of cellulose and modified cellulose samples; some differences observed in the FTIR spectra can be used to assess the success of the reaction of esterification using CA in both employed processes (ultrasonication and reactive extrusion). Compared to cellulose, in both group of modified samples, prepared by ultrasonication (US401minCA, US402minCA, US801minCA, and US802minCA) and reactive extrusion (EMCCA), it is possible to identify a new important band at 1735 cm^{-1} that can be associated with the C=O stretching of carbonyl in the ester bonds, confirming that esterification with CA occurred.

These results are consistent with those presented by other authors [25,28,30,48,49], who employed CA as an esterification agent for cellulose modification, these authors confirmed the success of the reaction employing FTIR spectra of the samples by observing the increased intensity of the bands at $1735\text{--}1738 \text{ cm}^{-1}$, free hydroxyls present on cellulose surface reacted with the carboxylic groups of CA forming ester bonds.

Romeo et al. [29] obtained citrate cellulose employing an eco-friendly process that involved the use of molten citric acid under solvent-free conditions at atmospheric pressure, and these authors reported that a strong band at 1736 cm^{-1} appears in citrate cellulose samples, and this strongly supports that cellulose esterification occurred after reaction with CA. They also proposed a reaction mechanism consisting in a simultaneous hydrolysis of cellulose with breaking of the intra- and intermolecular hydrogen bonds, followed by esterification of separate cellulose chains.

The A_{1735}/A_{2929} ratios of CA modified samples prepared by ultrasonication were higher than the ratio obtained for extruded sample (Figure 1), which is an indication that ultrasonication was more effective in the esterification of cellulose with CA at the studied conditions. Some studies in literature [25,42,48] also employed the same approach to indicate the esterification occurrence in cellulosic derivatives.

This same band (1735 cm^{-1}) was observed less intensely in the cellulose control sample (ECW), extruded without CA, and this can possibly be explained due to the thermomechanical treatment of cellulose during extrusion, and it could be attributed to the C=O group from the opened terminal glucopyranose rings, as observed by other authors [7] who obtained nanofibrillated cellulose using reactive extrusion.

3.3. X-ray Diffraction (XRD)

Figure 2 shows the diffractograms of cellulose and modified cellulose using both ultrasonication and reactive extrusion, and all samples resulted in similar patterns, with peaks compatible with the characteristic pattern of cellulose I at $2\theta = 15, 22, \text{ and } 34^\circ$ [6]. Both processes employed in this study (ultrasonication and reactive extrusion) resulted in any variation in the polymorph type of cellulose compared to the original raw material, which

demonstrated that these processes do not change the crystal organization of cellulose. Ramirez et al. [30] reported that the initial crystalline structure of cellulose remained unaffected after esterification.

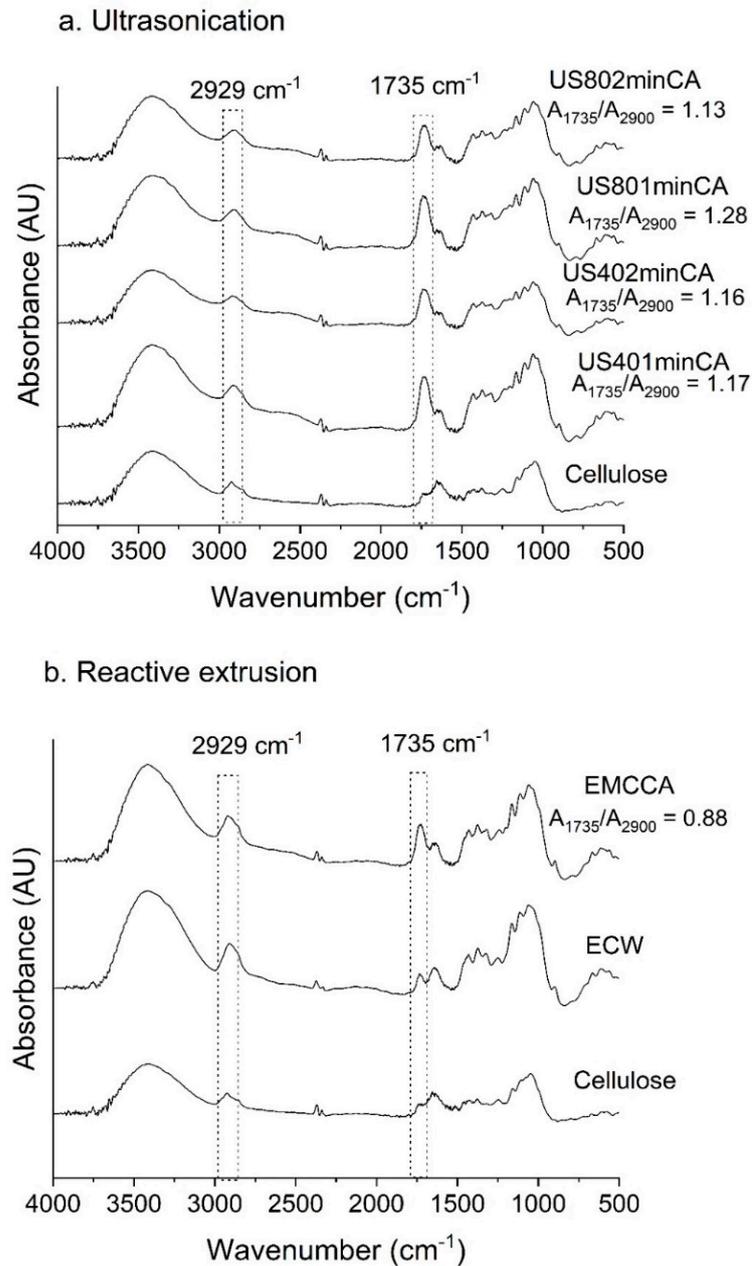


Figure 1. FT-IR spectra of cellulose and citric acid (CA) modified cellulose by (a) ultrasonication and (b) reactive extrusion.

CI values observed for cellulose samples subjected to ultrasonication ranged from 44% to 45%, very close values to the observed for unmodified cellulose (43%). Extruded samples (ECW and EMCCA) showed higher CI values, with 50% and 49%, respectively (Figure 2). Reactive extrusion is more aggressive than ultrasonication, combining thermomechanical and chemical pretreatments, which possibly resulted in the removal of amorphous fractions that were more susceptible to thermal degradation. Bhandari et al. [35] also reported an increase in crystallinity in carboxymethyl cellulose obtained by reactive extrusion.

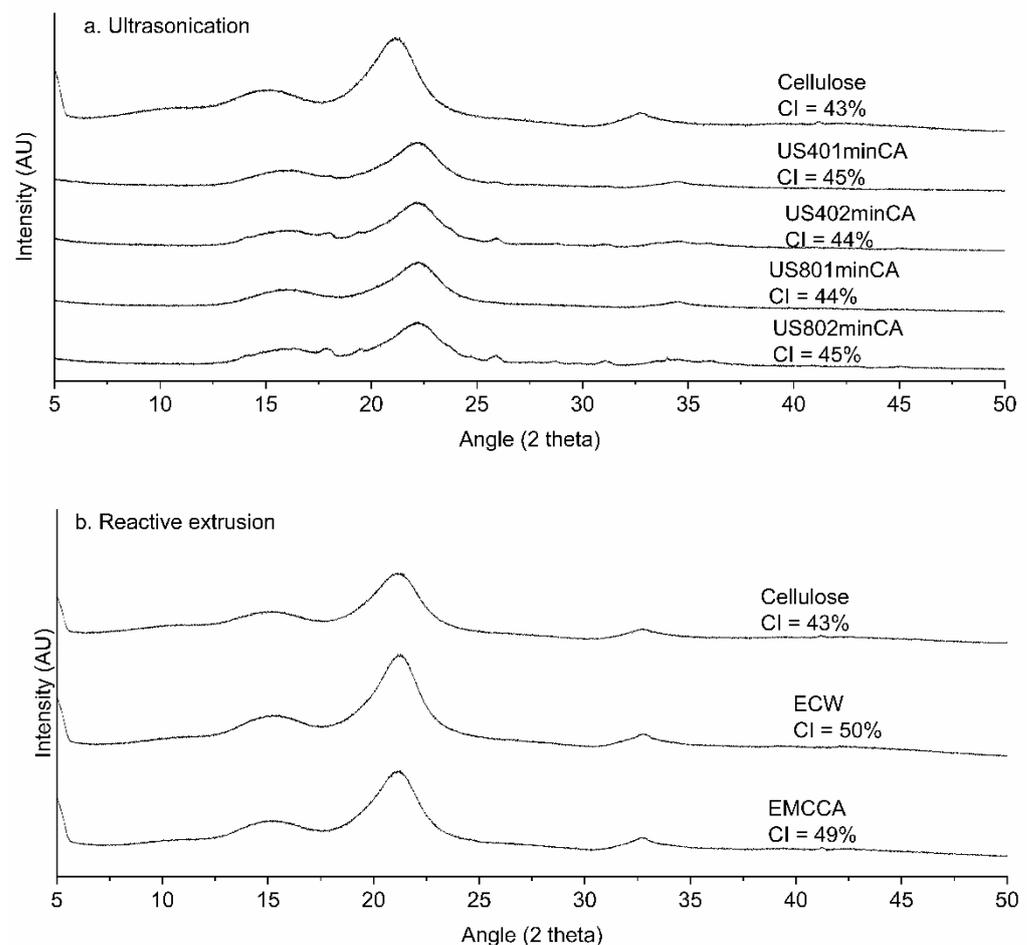


Figure 2. X-ray diffractograms of cellulose and CA modified cellulose by (a) ultrasonication and (b) reactive extrusion.

3.4. Thermogravimetric Analysis (TGA)

TGA and DTGA curves are shown in Figures 3 and 4. It was observed for all samples a first degradation stage at 50–100 °C, which can be attributed to the loss of water or other low-molecular-weight compounds [6,7]. Samples modified by ultrasonication assisted processes also presented weight losses around 190 °C (Figure 3), and according to Kaya [49], the weight loss at temperatures between 20 and 200 °C is related to the loss of surface and inner moisture by evaporation for non-crosslinked samples. Adewuyi and Pereira [50] reported that weight losses around 115–162 °C in esterified cellulose extracted from sesame seed can be assigned to the loss of volatile organic compounds.

For all cellulose and modified samples, the main weight loss occurred between 348 °C and 360 °C, and a second important peak was observed between 435 °C and 469 °C (Figures 3 and 4, Table 1), which can be attributed to the reactions of depolymerization, dehydration, and decomposition of glycoside units that occurred, which resulted in cellulose decomposition [6,49].

All modified samples presented higher T_{10} (temperature corresponding to 10% mass loss) and T_{max_2} higher than unmodified cellulose, which can be indicative that esterification of cellulose with poly (carboxylic acids) like citric acid, as observed by other authors [30,49,50], presents higher thermal stability of modified samples.

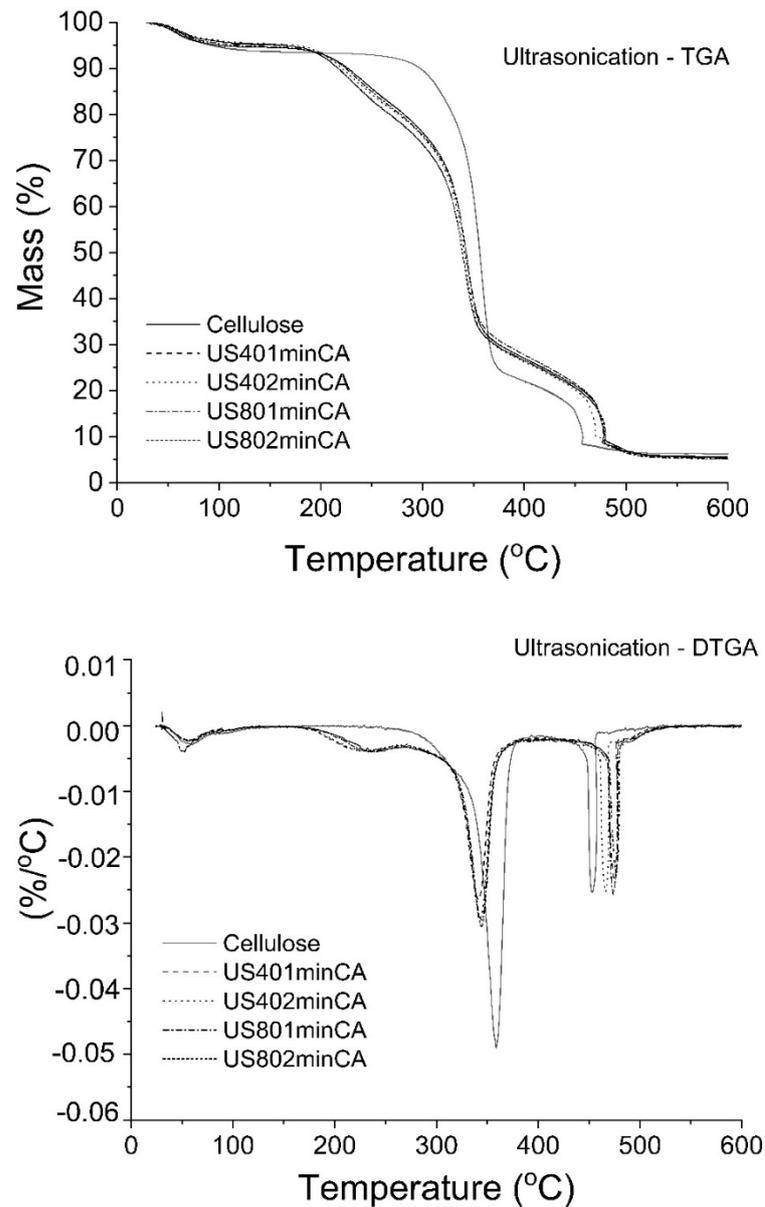


Figure 3. TGA/DTGA curves of cellulose and CA modified cellulose by ultrasonication.

Table 1. TGA parameters of cellulose and modified cellulose samples submitted to ultrasonication and reactive extrusion.

Sample	TGA Parameters		
	T_{max1} (°C)	T_{max2} (°C)	T_{10} (°C)
Cellulose	360	435	457
US401minCA	348	468	478
US402minCA	349	469	470
US801minCA	350	468	478
US802minCA	350	463	479
ECW	355	449	460
EMCCA	360	462	473

T_{max} = temperature corresponding to the maximum rate of mass loss, T_{10} = temperature corresponding to 10% mass loss.

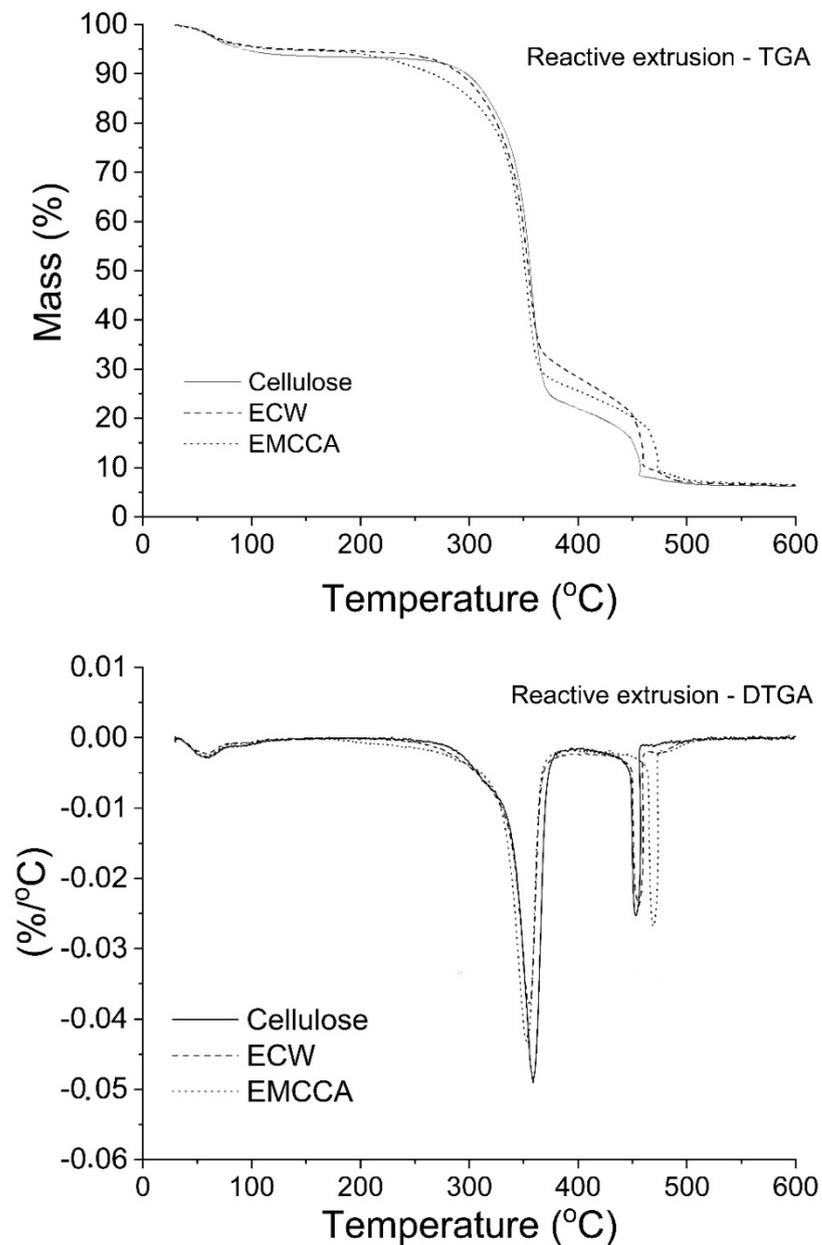


Figure 4. TGA/DTGA curves of cellulose and CA modified cellulose by reactive extrusion.

3.5. Differential Scanning Calorimetry (DSC)

Figure 5 presents the DSC curves of cellulose and modified cellulose samples. For both groups of samples, small endothermic events can be observed between 20 and 70 °C associated with water loss, which was also observed by other authors [25].

For all samples, it can be observed small endothermic events between 315 and 345 °C, which can be associated with the thermal decomposition of cellulose (Figure 5), as reported by other authors [51]. For unmodified cellulose, this peak presented higher intensity compared to modified samples, indicating higher thermal stability of modified samples, which is consistent with TGA results.

For all samples, it was observed the presence of small exothermic peaks around 350 °C, attributed mainly to exothermic reactions due to cellulose depolymerization. Other authors [52,53] also reported the same peaks in cellulosic-rich materials extracted from lignocellulosic residues.

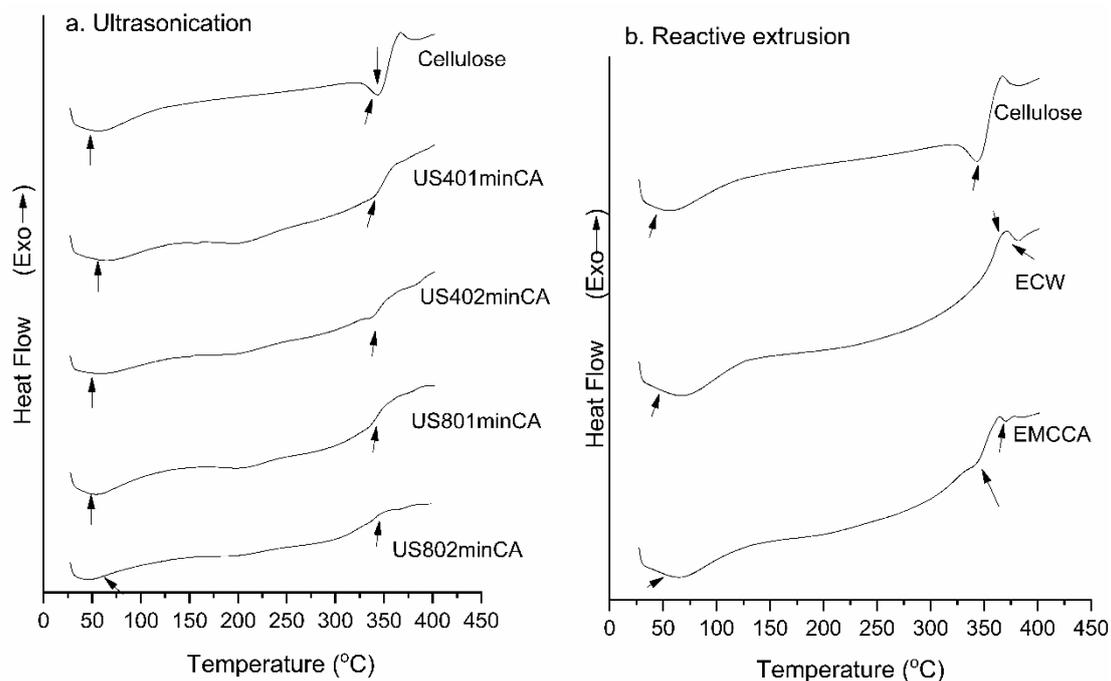


Figure 5. DSC curves of cellulose and CA modified cellulose by (a) ultrasonication and (b) reactive extrusion.

3.6. Scanning Electron Microscopy (SEM)

As observed in SEM micrography (Figure 6), raw oat hull presented a compact and uniform structure, a typical morphology of lignocellulosic materials, with the fibers bundled with the nonfibrous components (hemicellulose and lignin) [54]. After the removal of the outer layer composed of hemicellulose and lignin through the bleaching process with peracetic acid, cellulose showed a different morphology. This is due to the lignocellulosic complex being disrupted by the disintegration, resulting in long and individualized fibers of cellulose, agreeing with the results of other authors employing the same bleaching agent [6,7,55,56].

For both groups of samples esterified CA, individual fibers similar to unmodified cellulose were observed in the SEM micrographs, without visual differences between the different treatments used for modification (Figure 6).

3.7. Wettability

Wettability results can illustrate the tendency of a solvent to spread out and make intimate contact with a surface of interest [57] and the existence of polar and non-polar groups on the surface directly influences the wettability property [58].

As can be seen in Figure 7, the phenomenon of sample dispersion between a water/dichloromethane system showed a clear affinity of unmodified cellulose and ECW sample (control sample extruded in presence of water) for water (polar solvent). This is due to its hydrophilic character, totally contrary to the behavior of all samples modified with CA, which showed affinity to dichloromethane (non-polar solvent), showing the hygroscopic change suffered in cellulose by chemical modification, the new hydrophobic properties of the material being evident. According to Hubbe et al. [57], it is evident that polar hydroxyl groups at cellulose surfaces play a major role in wettability, and the substitution of these polar groups by less polar groups can affect wettability [39,59]. These results reinforced the data obtained by FTIR, which showed the introduction of CA in the cellulose structure.

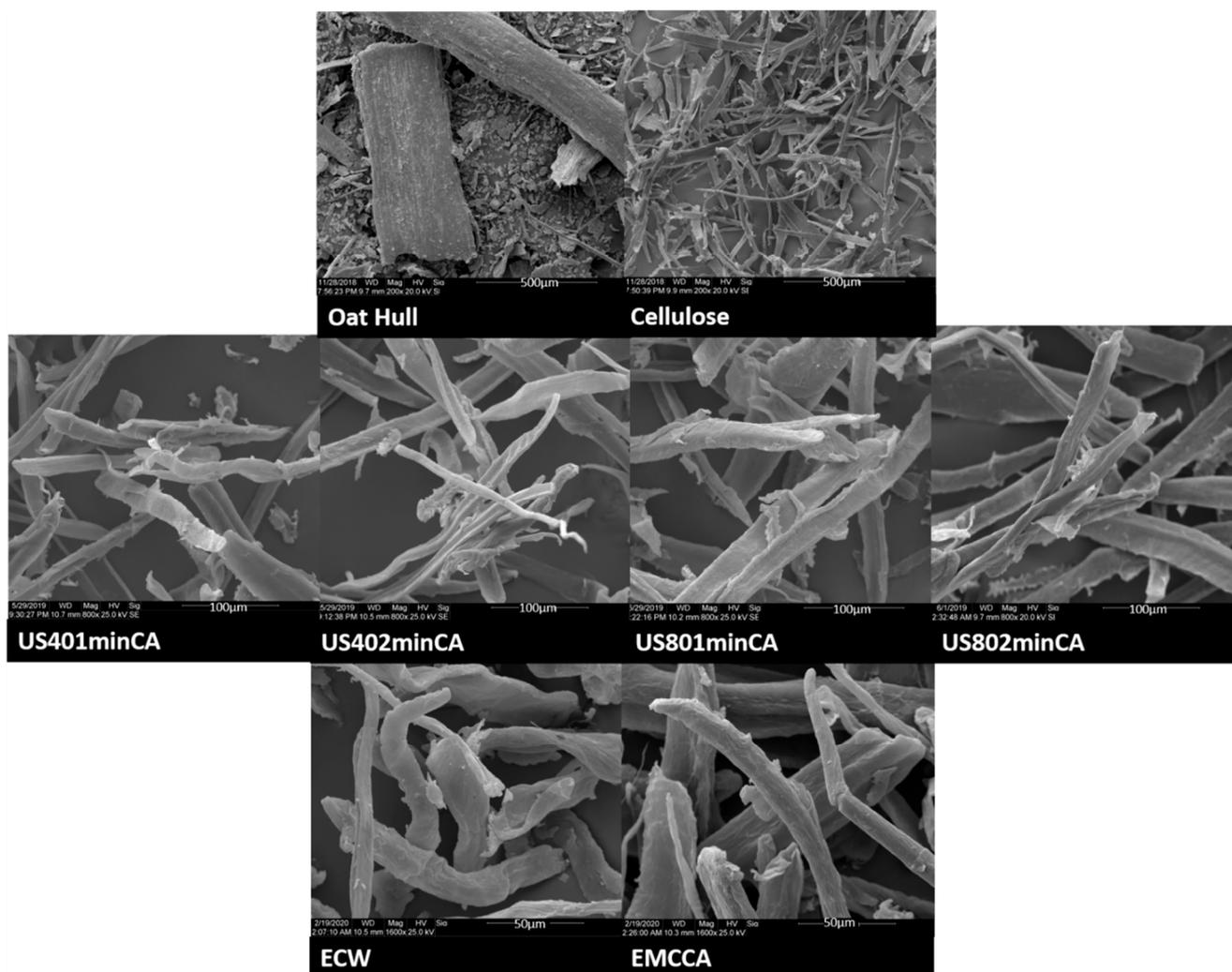


Figure 6. SEM of cellulose and CA modified cellulose by ultrasonication and reactive extrusion.

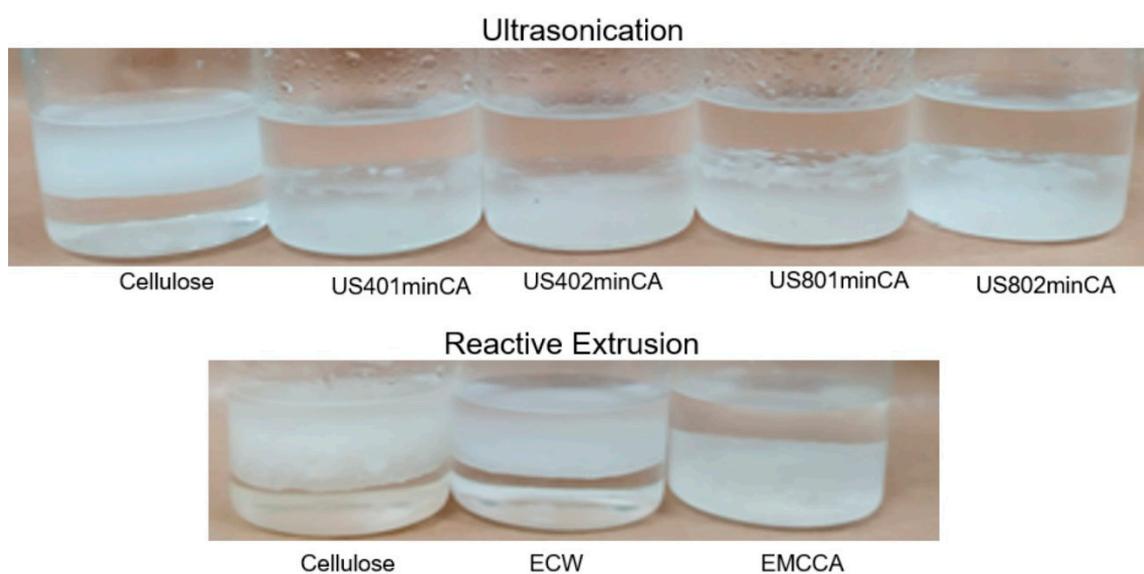


Figure 7. Dispersions of cellulose and CA modified cellulose by ultrasonication and reactive extrusion in a water/dichloromethane system.

3.8. Water Absorption Capacity (WAC) and Oil Absorption Capacity (OAC)

WAC and OAC results are presented in Table 2. There were observed changes for both groups of samples modified by ultrasonication and reactive extrusion assisted processes. For all modified samples, WAC values ranged from 1.63 to 1.71 (g/g) and these values were significantly lower when compared to unmodified cellulose (9.38 g/g) and ECW (control extruded sample, 7.75 g/g). Possibly, the ECW sample presented a lower WAC value than unmodified cellulose because the extrusion affected in some level the fiber surface; according to Vaidya et al. [38], the impact of torque action of extruder can affect some fibers properties. OAC increased in CA modified samples by 2 or 3 times when compared to cellulose and ECW samples (Table 2).

Table 2. Water and oil absorption capacities of cellulose and modified cellulose by ultrasonication and reactive extrusion.

Sample	WAC (g/g)	OAC (g/g)
Cellulose	9.38 ± 0.01 ^a	1.80 ± 0.01 ^d
US401minCA	1.69 ± 0.01 ^c	6.78 ± 0.30 ^{a,b}
US402minCA	1.68 ± 0.01 ^c	6.73 ± 0.30 ^{a,b}
US801minCA	1.70 ± 0.01 ^c	6.59 ± 0.04 ^b
US802minCA	1.71 ± 0.01 ^c	7.31 ± 0.12 ^a
ECW	7.75 ± 0.01 ^b	2.04 ± 0.50 ^d
EMCCA	1.63 ± 0.01 ^c	4.57 ± 0.32 ^c

^{a,b,c,d} Different letters in the same column indicate significant differences ($p \leq 0.05$) between means (Tukey's test).

Regarding to the differences between the two processes, it is possible to observe that there is a greater increase in hydrophobicity in the ultrasonicated samples which presented the higher OAC values (Table 2). These results agree with FTIR data that indicate that ultrasonication seemed to be more effective in the esterification of cellulose with CA at the studied conditions. These results corroborate that the modified cellulose had its hydrophilic character altered by the decrease of free hydroxyl groups on the cellulose surface by reaction with CA. Adewuyi and Pereira [50] modified cellulose with suberic acid and reported that the improved hydrophobicity of modified samples can be demonstrated by the reduction in WAC and increasing in the OAC.

3.9. Moisture Sorption Isotherms

Moisture sorption isotherms and parameters of the GAB model are shown in Figure 8 and Table 3, respectively. Modified samples show similar patterns, with a practically linear increase in the moisture content due to the adsorption of water molecules that are partially bound [60].

Table 3. GAB model parameters of cellulose and cellulose samples modified by ultrasonication and reactive extrusion.

Sample	m_0	C	K	r^2
Cellulose	39.19	1.44	0.23	0.99
US401minCA	11.78	1.71	0.40	0.98
US402minCA	20.42	1.53	0.26	0.98
US801minCA	16.86	1.54	0.31	0.98
US802minCA	19.11	1.47	0.28	0.98
ECW	16.67	1.92	0.39	0.99
EMCCA	5.68	2.68	0.55	0.98

$M = m_0 C K a_w / (1 - K a_w) (1 - K a_w + C K a_w)$, where M is the equilibrium moisture content at a water activity (a_w), m_0 is the monolayer value (g water/100 solids), and C and K are the GAB constants.

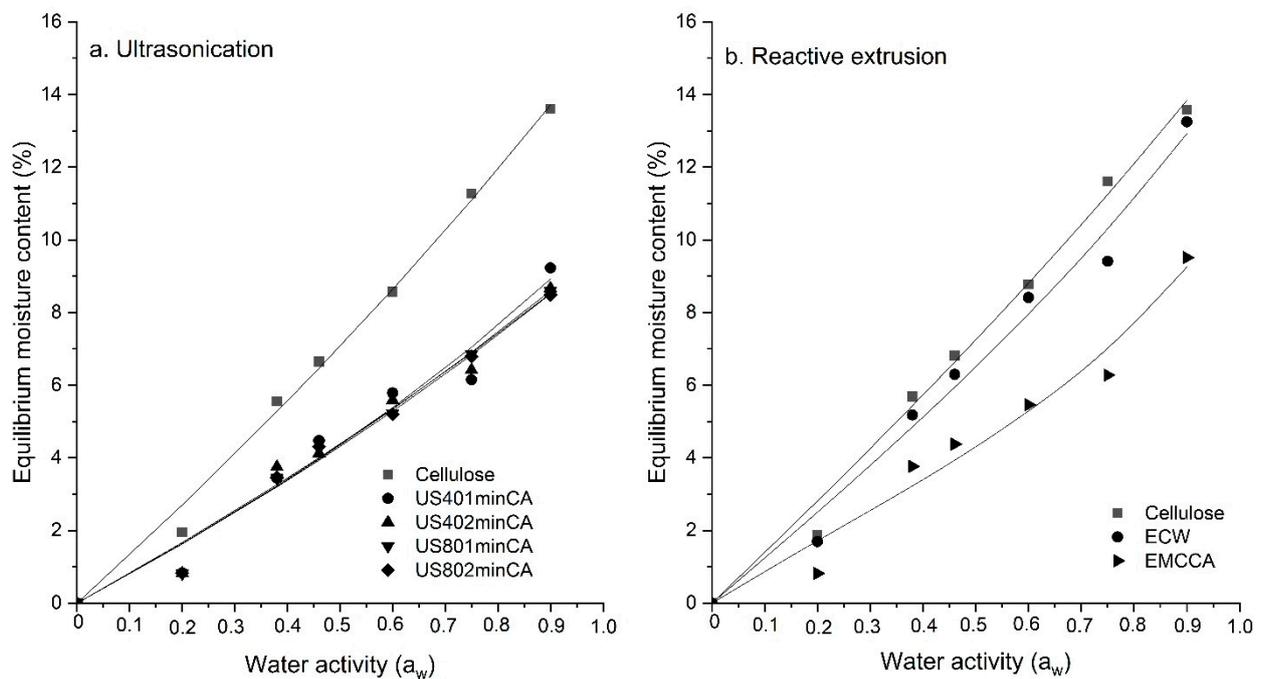


Figure 8. Moisture sorption isotherms of cellulose and modified cellulose by (a) ultrasonication and (b) reactive extrusion. Lines are derived from GAB models.

The monolayer value (m_0) can be defined as the limit of the model between chained water and free water, being an indicator of the maximum amount of water that can be adsorbed in a single layer per gram of dry matter. Both modification processes showed similar behaviors concerning the m_0 (Table 3), with the higher value obtained for cellulose sample. The EMCCA sample showed the lowest m_0 value (5.68 g water/100 g solids) followed by US401minCA sample (11.78 g water/100 g solids). These results indicated a change in the adsorption properties of cellulose by reaction with CA.

4. Conclusions

Modified cellulose samples with increased hydrophobicity were obtained through esterification with citric acid employing ultrasonication and extrusion assisted processes. FTIR confirmed the modification of the material for all tested conditions by the appearance of a new band at 1735 cm^{-1} . All modified samples showed a reduced water absorption capacity with increased oil absorption, and all samples presented higher affinity for low polar solvents.

Ultrasonication and reactive extrusion were effective in the obtainment of esterified cellulose with citric acid; however, ultrasonication seemed to be more effective, with the advantages of reducing the processing times and low generation of effluents when compared to the conventional processes employed to obtain esterified cellulose, being considered promising green alternatives for this purpose.

Author Contributions: Conceptualization, S.M. and G.A.G.G.; methodology, S.M., G.A.G.G., J.M., B.M.M., and J.O.F.K.; formal analysis, S.M. and G.A.G.G.; investigation, S.M., G.A.G.G., J.M., B.M.M., and J.O.F.K.; writing—original draft preparation, S.M. and G.A.G.G.; writing—review and editing, S.M. and G.A.G.G.; supervision, S.M. All authors have read and agreed to the published version of the manuscript.

Funding: This work was supported by CAPES-Coordenação de Aperfeiçoamento de Pessoal de Nível Superior for the grant to the postgraduate students.

Informed Consent Statement: Not applicable.

Acknowledgments: The authors would like to thank the Universidade Estadual de Londrina-UEL facilities at the Multiuser Laboratories Center (CMLP-UEL FINEP), where X-ray, FT-IR, and microscopy analyzes were performed.

Conflicts of Interest: The authors declare no conflict of interest.

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