

LOW-COST CARBOXYMETHYL HOLOCELLULOSE AND CARBOXYMETHYL CELLULOSE FROM WHEAT STRAW

NAJAH LARIBI,^{*} SAMAH MAATOUG,^{*} ZAYNEB JEBALI,^{**} RIADH ZOUARI,^{*}
HATEM MAJDOUB^{**} and MORCHED CHEIKHROUHOU^{*}

^{*}University of Monastir, ISET Ksar Hellal, Laboratory of Textile Engineering, B.P. 68,
Ksar Hellal, 5070, Monastir, Tunisia

^{**}University of Monastir, Faculty of Sciences of Monastir, Laboratory of Interfaces and Advanced Materials,
Avenue of the Environment, 5019, Monastir, Tunisia

✉ Corresponding author: Hatem Majdoub, hatemmajdoub.fsm@gmail.com

Received October 14, 2019

The chemical composition of Tunisian wheat straw was determined, demonstrating that this biomass is rich in α -cellulose and holocellulose with values of 41.4% and 72%, respectively. Holocellulose and cellulose were extracted from this biomass and converted into carboxymethyl holocellulose (CMH) and carboxymethyl cellulose (CMC), respectively, with different degrees of substitution (DS) by varying the concentration of the etherifying agent. The physicochemical properties and the morphology of the different products synthesized were studied using Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), thermogravimetric analysis (TGA) and scanning electron microscopy (SEM) techniques. The rheological behavior of all the CMH and CMC samples was also considered and the effect of the DS on the apparent viscosity of the materials obtained was studied. The results demonstrated that all the carboxymethylated products exhibited non-Newtonian thixotropic behavior and that the apparent viscosity of the aqueous solutions of CMH and CMC depended on the DS. We concluded that CMH and CMC with appropriate degrees of substitution have great potential for many applications.

Keywords: wheat straw, holocellulose, cellulose, carboxymethylation, degree of substitution, rheological properties

INTRODUCTION

The depletion of petroleum-based reserves, the rising cost and the associated environmental problems, such as global warming, are the most important reasons why scientific research has been directed towards further exploitation of natural sustainable materials, which are composed of cellulose, hemicelluloses and lignin.^{1,2} Lignocellulosic biomass, which is the most abundant and bio-renewable biomass on earth, has various advantages, such as renewability, biodegradability and environmental friendliness; therefore, it can be used as a suitable alternative for petroleum-based materials as means of overcoming environmental problems.

Wheat straw (*Triticum aestivum* L.), the residue after wheat harvest, is produced in large quantities all over the world. Even with the many existing uses for wheat straw, in many regions and countries around the world there is a surplus of wheat straw. Field burning of wheat straw to dispose of this surplus is practiced well.^{3,4} In

Tunisia, wheat accounts for 60% of the national cereal production.⁵ In 2015, 1.3 million tons of durum wheat was produced⁶ and, at a conservative straw to grain ratio of 1:1, the production of wheat straw was probably of the order of 1.3 million tons also. The wheat straw is an extremely low-cost material, which is usually used for cattle feed.

Wheat straw is a biocomposite that consists mainly of cellulose (34 to 40%), hemicelluloses (30 to 35%), and lignin (14 to 15%),⁷ and this relatively high amount of cellulose emphasizes the need to use this material as a new polymer for industries. In other words, cellulose represents almost one-third of the weight of all trees, vines, grasses and straws. In addition, it is constantly renewed by photosynthesis and growth, with an annual production estimated to be over 7.5×10^{10} tons.⁸ This represents a vast potential feedstock for a number of industries, and has generated a great deal of research interest.

The use of cellulose and its derivatives in a diverse array of applications, such as fibers, films, coatings, plastics, suspension agents and composites, continues to grow on a world-wide basis. As a regenerative raw material, cellulose can be also converted by chemical modification into water-soluble derivatives. One modification reaction of interest is carboxymethylation. Carboxymethyl cellulose (CMC) is water-soluble cellulose ether produced by the partial substitution of the hydroxyl groups of cellulose with ionic hydrophilic moieties. The average number of the hydroxyls in the glucose unit that has reacted is called the degree of substitution (DS) and CMCs are categorized accordingly. The major markets for CMC are detergents, foods and pharmaceuticals, textiles, drilling muds, paper sizing and coating, and miscellaneous other applications, including adhesives, ceramics, latex paints, and welding rod coatings. Carboxymethyl cellulose is used in detergents as a soil-suspending and anti-redeposition agent, in textiles as a warp size material, in paper and paper products for surface sizing, in coatings for rheology control and water retention, and in drilling muds as a fluid-loss agent. Those properties have made CMC the most frequently produced and widely used industrial cellulose ether.⁹

Since 1980, efforts have been made to search for cheaper alternatives to expensive cotton, such as various lignocellulosic biomasses (rich in cellulose), for CMC production. Many lignocellulosic raw materials have been employed for the preparation of CMC: for example, sugar beet pulp,¹⁰ corn husk,¹¹ rice straw,¹² sugarcane straw,¹³ sago waste,¹⁴ wheat straw, barley straw and rice hull.¹⁵ However, only few studies have addressed the extraction and the carboxymethylation of holocellulose.

In this work, we chose Tunisian wheat straw as an inexpensive feedstock for bio-based materials since this biomass is very rich in cellulose and, especially, in holocellulose. The first objective of this study was to determine the chemical composition of this agricultural by-product.

The second one was to extract both holocellulose and cellulose from wheat straw and to convert them applying the carboxymethylation reaction (with different degrees of substitution, by varying the concentration of the etherifying agent).

EXPERIMENTAL

Materials and reagents

Wheat straw was acquired from a farm in Beja (North West Tunisia). This agricultural residue was first cut into small pieces and dried in an oven at 50 °C for 24 h, then it was milled in a kitchen blender in order to obtain fine powder. The powder particles under 60 mesh size were collected.

All reagents and chemicals used were acquired from Sigma-Aldrich and used as received without purification.

Chemical composition

The chemical composition of the Tunisian wheat straw was determined using the standard Technical Association of the Pulp and Paper Industry (TAPPI) methods for different components, namely, cold and hot water solubility (T207 cm-08), 1% sodium hydroxide solution solubility (T212 om-12), ethanol-toluene solubility (T204 cm-07), ash (T211 om-93), α -cellulose (T203 cm-99) and Klason lignin (T222 om-88). The holocellulose was determined by the method described by Wise *et al.*¹⁶ and the rate of hemicelluloses was calculated as the difference between the holocellulose and α -cellulose. In each case, the average of three tested samples was reported.

Isolation of holocellulose and cellulose from wheat straw

The holocellulose was extracted from wheat straw according to the acid-chlorite method, as reported by Wise *et al.*¹⁶ with some modifications. For holocellulose extraction, the dried and sieved wheat straw (10 g) was first treated with 200 mL of H₂O at 75 °C for 2 h. Further, the water-soluble free sample was delignified with 1.7% sodium chlorite at pH 3.5-4.0, adjusted with 6M acetic acid, at 75 °C for 2 h (the delignification was repeated 3-4 times until the product became colorless).

For the preparation of cellulose, the holocellulose obtained was treated with 10% potassium hydroxide for 16 h at room temperature in order to solubilize the hemicellulose fractions. The holocellulose and cellulose obtained were washed with a copious amount of distilled water until the filtrate became neutral, followed by drying at ambient temperature.

Carboxymethylation of cellulosic fractions

Holocellulose and cellulose isolated from the wheat straw were transformed into CMH and CMC, respectively, in two steps (Fig. 1): alkalization, followed by etherification. The carboxymethylation procedure described by Mansouri *et al.*¹⁷ was applied in this study with some modifications. In the alkalization pre-treatment, about 10 g of unmodified material was weighed and added to 60 mL of 1-butanol, followed by 60 mL of 40% aqueous sodium hydroxide solution. Then, the mixture was stirred for 12 h at 60 °C in order to convert the hydroxyl groups

to alcoholate groups. After the alkali treatment, the etherification reaction was conducted by adding the desired amount of monochloroacetic acid (MCA). The etherification reaction lasted for 6 h at 60 °C. Then, the slurry was neutralized using glacial acetic acid until the pH reached 6-8. The product thus obtained was suspended in 800 mL of ethanol and, in order to obtain CMH and CMC derivatives free from salts, the sample was washed five times using a 70% ethanol solution. The different products obtained were dried in an oven at 50 °C for 24 h and stored in polyethylene bags.

Using the above procedure, three different derivatives per each initial product (designated CMH1, CMH2, CMH3, CMC1, CMC2 and CMC3) were prepared, as detailed in Table 1.

Analysis and measurement

The Tunisian wheat straw, the holocellulose and the cellulose extracted were characterized by means of FTIR, XRD, TGA and morphological analysis.

The prepared carboxymethyl holocellulose and carboxymethyl cellulose were characterized in terms of

DS, CMC yield and also by FTIR, XRD, TGA, morphological and rheological analyses.

FTIR spectroscopy

FT-IR spectroscopy has been extensively used in cellulose research, since it represents a relatively easy method of obtaining information on the chemical changes that occur during various chemical treatments. The spectra were measured in the region 400-4000 cm⁻¹ in a spectrophotometer (Perkin Elmer UATR Two).

X-ray diffraction

The X-ray diffractograms of untreated wheat straw, holocellulose, cellulose, CMH and CMC were recorded on a PANalytical X'Pert Pro-MPD powder diffractometer. The crystallinity index (CrI) of wheat straw, holocellulose and cellulose was calculated using the following equation:^{18,19}

$$CrI(\%) = \frac{(I_{002} - I_{am})}{I_{002}} \times 100 \quad (1)$$

where I_{002} is the height of the 002 peak, which represents both crystalline and amorphous material and I_{am} is the lowest height between the 002 and 110 peaks, which represents only the amorphous material.

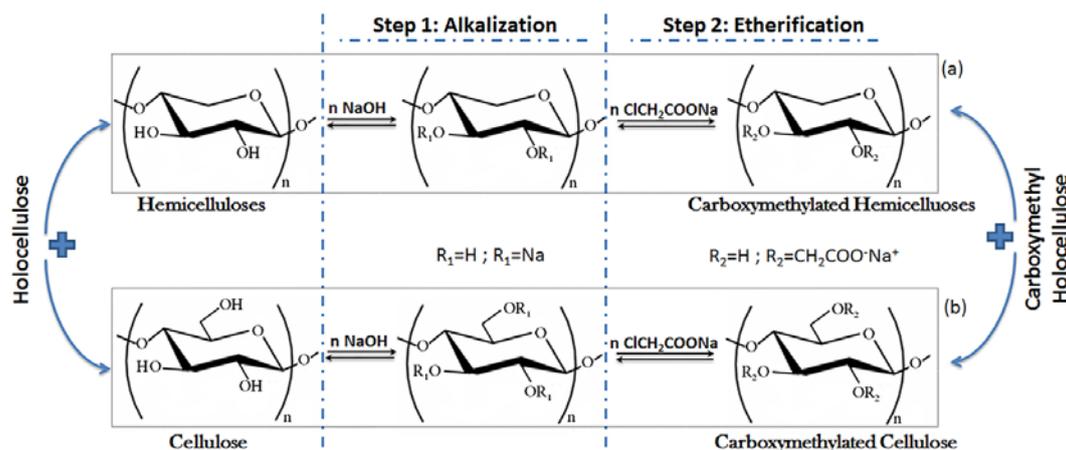


Figure 1: Schematic representation of (a) synthetic route of carboxymethylation of hemicelluloses and (b) synthetic route of carboxymethylation of cellulose; the carboxymethylation of holocellulose includes both hemicelluloses and cellulose carboxymethylation

Table 1
CMH and CMC preparation conditions, their degrees of substitution and their yields

Reaction	Weight of dried product (g)	Weight of MCA (g)	Designation	DS	CMH and CMC yield (%)
Holocellulose carboxymethylation	10	10	CMH1	0.78*	131.6
	10	15	CMH2	1.04*	139.8
	10	25	CMH3	1.37*	143.2
Cellulose carboxymethylation	10	10	CMC1	0.43	123.6
	10	15	CMC2	0.88	135.4
	10	25	CMC3	1.23	141.4

*Estimation of DS

Thermogravimetric analysis (TGA)

The thermal stability of the different materials was assessed using a NETZSCH-STA 449 F1 Jupiter thermogravimetric analyzer. All the measurements were carried out under nitrogen atmosphere, with a gas flow of 10 cm³/min, by heating the samples at a heating rate of 10 °C/min from room temperature to 600 °C.

Field emission scanning electron microscopy (FE-SEM)

A field emission scanning electron microscope (JOEL JSM-5400) was used to follow up the surface modification of the untreated wheat straw, holocellulose, cellulose fibers, carboxymethyl holocellulose and carboxymethyl cellulose (with different degrees of substitution). The acceleration voltage used was 15 kV. Prior to the analysis, the samples were coated with an ultrathin gold layer in a sputter coating system (JFC-1100E Ion Sputtering Device).

CMC and CMH yield

The CMC/CMH yield was quantified on a dry weight basis. In order to determine the yield value, the net weight of the dried CMC (respectively, CMH) synthesized was divided by the weight of dried cellulose (respectively, holocellulose) as follows:^{11,20}

$$\text{CMC/CMH yield (\%)} = (m_2/m_1) * 100 \quad (2)$$

where m_2 is the weight of the dried CMC (respectively, CMH) synthesized and m_1 is the weight of the dried cellulose (respectively, holocellulose).

Determination of the degree of substitution (DS) of CMC and CMH

An amount of 5 g of CMC (or CMH) was added to 200 mL HNO₃-CH₃OH (1:1 v/v). The mixture was shaken and was kept for 3 h. The excess of acid was washed with a 70% methanol solution until neutrality. Thereafter, 2 g of dried sample was dissolved in 200 mL of H₂O and 30 mL of 1N NaOH mixture. Then, the solution was titrated with 1N HCl. The DS of CMC and CMH was determined by the following equations:^{10,13}

$$\text{DS} = (0.162 * A) / (1 - (0.058 * A)) \quad (3)$$

$$A = [(B * C) - (D * E)] / F \quad (4)$$

where A: equivalent weight of alkali required per gram of sample, B: amount of NaOH solution (mL), C: normality of NaOH solution (N), D: amount of HCl solution (mL), E: normality of HCl solution (N), F: sample weight (g).

Since carboxymethyl holocellulose is a mixture of carboxymethylated cellulose and hemicelluloses, the DS determination formula described above (Eq. 3) can only give an indication of the DS values of CMH. That is why, in the present work, the determined values of the degree of substitution of carboxymethyl holocellulose were estimated.

Rheological measurements of CMH and CMC

Rheological measurements were carried out using a controlled speed rotating rheometer (RC30 Rheotec), using a cone and plate geometry. It is well known in the literature that the rheological properties of CMC depend strongly on concentration and on the temperature during measurement.^{21,22} For this, aqueous solutions of CMH and CMC were prepared in 4% w/v concentration and all the experimental measurements were conducted at a controlled temperature of 25 °C ± 1 °C. The apparent viscosity (η) at various shear rates was calculated from the shearing stress (τ) and the shear rates (D), as follows:¹²

$$\eta = \tau / D \quad (5)$$

RESULTS AND DISCUSSION**Characterization of extracted cellulose and holocellulose**

The chemical composition of Tunisian durum wheat straw, used as an agricultural by-product, was determined and presented in Table 2. The data show that the material studied presents a high amount of α -cellulose (41.4 g per 100 g of dry material) against a low amount of lignin (12 g per 100 g of dry material). It is also obvious that the holocellulose content in the Tunisian wheat straw is quite high (72 g per 100 g of dry material). The high levels of cellulose and holocellulose in this biomass make it a good source for cellulose and holocellulose extraction.

Table 2
Chemical composition of Tunisian durum wheat straw in w/w (%) compared with data from previously published studies

Composition	Tunisian durum wheat straw	Khiari <i>et al.</i> ³⁵
Solvent extractives	6.4±1	4.6-9.2
Hot water solubility	12±0.8	14
1% NaOH solubility	39±0.7	41-42.8
Ash	4±0.5	4-9
Klason lignin	12±0.8	11-21
Holocellulose	72±1.2	-
α -Cellulose	41.4±1	33-45.5

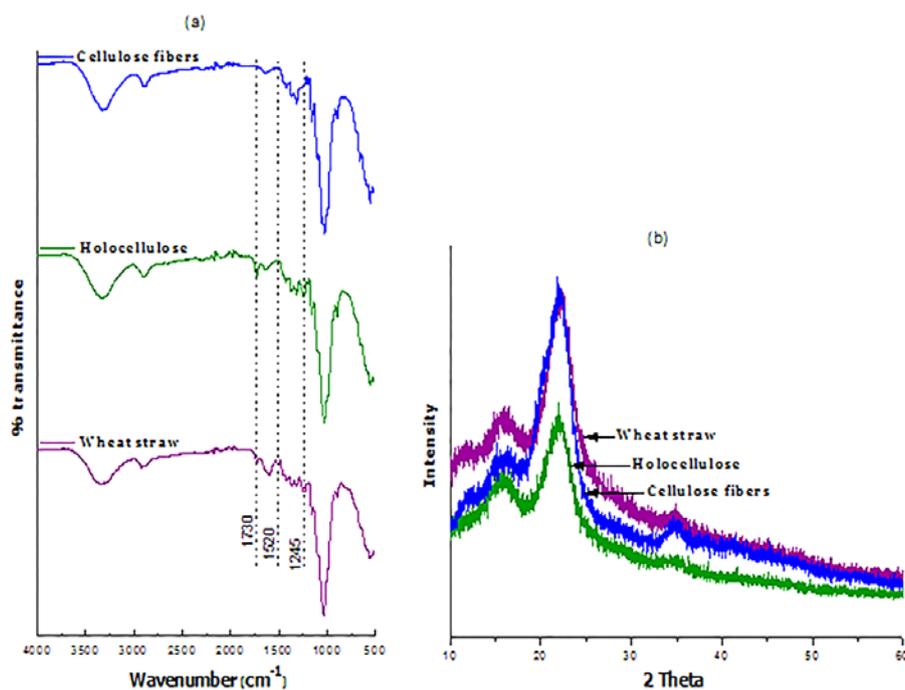


Figure 2: Characterization of Tunisian wheat straw, holocellulose and cellulose fibers by (a) FTIR and (b) XRD

The characterization of the holocellulose and cellulose extracted from this biomass was done by FTIR spectroscopy, X-ray diffraction, thermogravimetric and morphological analyses. The differences between the wheat straw powder, holocellulose and cellulose can be seen in all the characterizations carried out.

FTIR spectroscopy

The FTIR spectra of wheat straw, holocellulose and cellulose fibers are shown in Figure 2.

The main results revealed the disappearance of the peak at 1520 cm^{-1} corresponding to C=C stretching of the aromatic ring, confirming the total removal of lignin after the delignification process. The bands at 1730 and 1245 cm^{-1} , assigned to the acetyl ester groups of the hemicelluloses, decreased in intensity in holocellulose and disappeared in the cellulose fibers after the treatment with KOH. The band at 1640 cm^{-1} is assigned to the C=C stretching of the aromatic rings of lignin in the case of the untreated wheat straw, but it is also present in the spectra of holocellulose and cellulose; in this case, this band is related to the bending mode of adsorbed water. The characteristic band vibration of the glycosidic ring appeared in the $1100\text{--}1000\text{ cm}^{-1}$ region is characteristic of the β -1,4

glycosidic linkage between the sugar units. The dominant absorption peaks around 3338 and 2918 cm^{-1} are attributed to the stretching of --OH groups and the C-H bond in --CH_2 , respectively.²³

XRD analysis

The chemical treatment to which the wheat straw fibers were subjected resulted in changes in X-ray diffraction patterns (Fig. 2), which indicate modifications in the crystalline structure of durum wheat straw upon chemical conversion to holocellulose and to cellulose. The crystallinity index (CrI) of the three samples was calculated and the value was found to be 46%, 51.23% and 56.63% for untreated wheat straw, holocellulose and cellulose fibers, respectively. The results show that, during the chemical extraction of the holocellulose and/or the cellulose from untreated wheat straw, the crystallinity of the samples increases due to the removal of amorphous non-cellulosic compounds, such as lignin and hemicelluloses, during the bleaching and the alkali treatments carried out in the extraction process.

It is also observed that the cellulose extracted from wheat straw (Fig. 2b) had a type I crystal structure (characteristic peaks at $2\theta=16.0^\circ$, 22.6° and 34.7°), corresponding to the native crystal structure of cellulose.²⁴

TGA

The TGA curves of untreated wheat straw, holocellulose and cellulose extracted are presented in Figure 3. For all the materials, it is observed that an initial low weight loss occurs in the range of 35-150 °C, owing to the dehydration of adsorbed moisture.²⁵

Many studies related to the decomposition of lignocellulosic materials^{26,27} reported that the decomposition temperature of hemicelluloses, cellulose and lignin were in the ranges of 200-315, 315-400 and 160-900 °C, respectively, and this is due to the differences in their chemical structures. Looking at the TGA curve for untreated wheat straw, it is obvious that the decomposition of this biomass indicates several stages, showing the presence of different components (moisture, hemicelluloses, cellulose and lignin).

The decomposition temperatures of the wheat straw, holocellulose and cellulose were 265.19,

295.89 and 335.34 °C, respectively, proving that the thermal stability of the material increased after the chemical treatments applied during cellulose extraction. At last, the residue still present at 600 °C for the extracted cellulose is of only 1.56%, while it amounted to 4.43% for the wheat straw and to 4.11% for the holocellulose.

SEM analysis

Characterizing substances by scanning electron microscopy has become an efficient technique to follow the changes that occur in the surface morphology of a given material due to chemical reactions. Figure 4 presents the SEM micrographs of wheat straw fiber surfaces at different steps of chemical extraction. These micrographs show significant changes in the fiber surface morphologies. The wheat straw powder (Fig. 4a) consists of fiber bundles, rich in non-cellulosic particles surrounding the surface of cellulose fibers and binding them together.

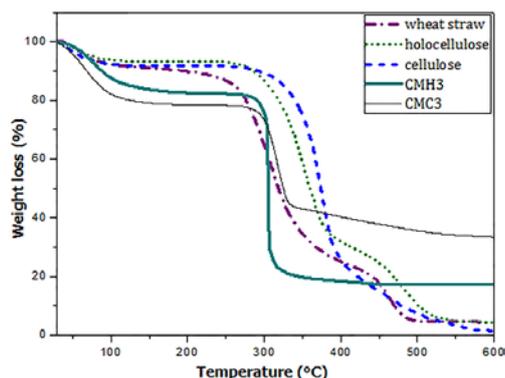


Figure 3: TGA curves for wheat straw, holocellulose, cellulose fibers, CMH3 and CMC3

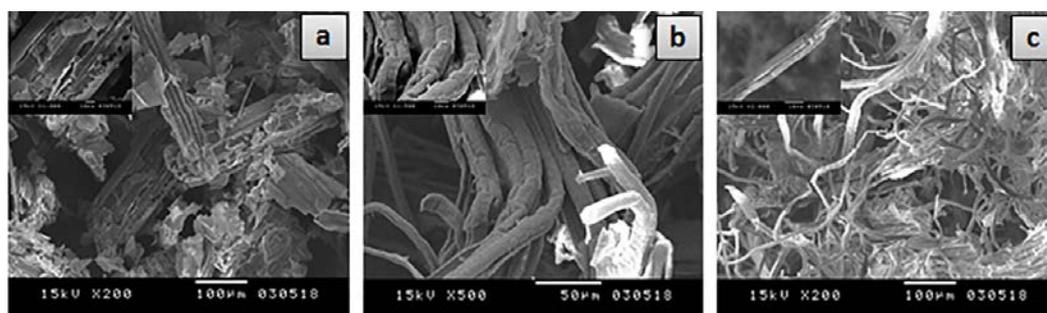


Figure 4: SEM of (a) untreated wheat straw; (b) holocellulose and (c) extracted cellulose fibers

The holocellulose (Fig. 4b), with its cleaner surface, indicates the removal of lignin and some other extractives during delignification with acidified sodium chlorite. It can be seen in Figure 4c that, after the alkali treatment, the hemicelluloses and other residual extractives are

removed from the holocellulose, and the material turns from fiber bundles into individual fibers with reduced diameters.

Carboxymethylation of cellulose and holocellulose

Cellulose and holocellulose extracted from Tunisian wheat straw were exposed to the carboxymethylation reaction, as already described above. The holocellulose is a combination of hemicelluloses (mixture of polysaccharides) and cellulose (a glucan polymer) and the carboxymethylation of this material includes two types of reactions: hemicellulose carboxymethylation (Fig. 1a) and cellulose carboxymethylation (Fig. 1b). The hemicelluloses were presented in Figure 1 by an idealized xylan structure, given that xylans are the predominant hemicellulose polysaccharides in herbaceous biomass.²⁸

In the present work, only the etherifying agent was selected to be variable in order to obtain carboxymethyl cellulose (CMC) and carboxymethyl holocellulose (CMH) with different degrees of substitution. The effect of monochloroacetic acid (ClCH_2COOH) concentration on the degree of substitution (DS) is presented in Table 1, and the data show that, by increasing the MCA concentration, the DS of the prepared materials increases evidently. For instance, when the concentration of MCA was 10 g/10 g of dry cellulose (respectively, holocellulose), the DS was 0.43 (respectively, 0.78), whereas the DS increased to 1.23 (respectively, 1.37) when the amount of MCA was increased to 25 g/10 g of cellulose (respectively, holocellulose). This increase is possibly due to the larger availability of the acetate ions at higher concentrations in the proximity of cellulose or hemicellulose molecules,²⁹ obviously, in the case of holocellulose, which is a mixture of cellulose and hemicelluloses.

The yield of carboxymethyl cellulose and carboxymethyl holocellulose synthesized is also presented in Table 1. The results provided indicate that increasing the MCA concentration caused the percent yield of CMC (respectively, CMH) to increase. This can be explained by the increase in the substitution of protons of the hydroxyl groups of cellulose and hemicelluloses (in the case of holocellulose), as the MCA concentration increases, by the carboxymethyl groups with a higher molecular mass. Therefore, the higher the number of carboxymethyl groups attached to the cellulose or holocellulose, the higher the mass of the carboxymethylated

material and thus, the percent yield increases evenly.

FTIR spectroscopy

The FTIR spectra of the CMH and CMC samples prepared are shown in Figure 5 and all the spectra demonstrate that the chemical carboxymethylation of cellulose and holocellulose has been successful. This is confirmed by the appearance of an extra absorption band centered at 1595 cm^{-1} attributed to the stretching vibration of the $\text{C}=\text{O}$ carboxylate groups ($-\text{COO}^-\text{Na}^+$).^{30,31} In Table 3, the main FTIR spectral data of the prepared CMC and CMH are grouped.

XRD analysis

The crystallographic behavior of CMH and CMC was studied by X-ray diffraction (XRD) and presented in Figure 5. It is noted that the three typical crystalline peaks of cellulose I (already observed in Fig. 1) disappeared after carboxymethylation, which indicates that the products obtained have an amorphous structure. This refers to the carboxymethyl groups that substitute the hydrogens atoms of the hydroxyl groups existing in cellulose and holocellulose.³²

The X-ray patterns of carboxymethyl cellulose and carboxymethyl holocellulose revealed that all the carboxymethylation reactions were successful by the presence of a peak around $2\theta = 21^\circ$. This finding is in agreement with the XRD results reported for various grades of CMC in the literature.^{33,34}

TGA

As may be noted in Figure 3, introducing carboxymethyl groups in the cellulose and hemicelluloses chains reduced the thermal stability of the polymer. As expected, the conversion of cellulose to CMC and holocellulose to CMH through the carboxymethylation reaction modifies the molecular structure and bonding energy of the material, and then affects its thermal behavior. In this study, we chose to study only the thermogravimetric properties of carboxymethylated samples with the highest degrees of substitution, namely, CMC3 and CMH3.

The first weight loss, associated with the dehydration of the samples, is remarked on the TGA curves in the temperature range from 30 to $180\text{ }^\circ\text{C}$ for CMC3 and CMH3, and was calculated to reach approximately 21% and 17%, respectively. This high water content in the

synthesized materials is due to their strong hydrophilicity. The hydrogen bonds formed between the water molecules and the polymer

chains cannot be neglected, they were probably formed between H₂O and hydrophilic OH and COONa groups.

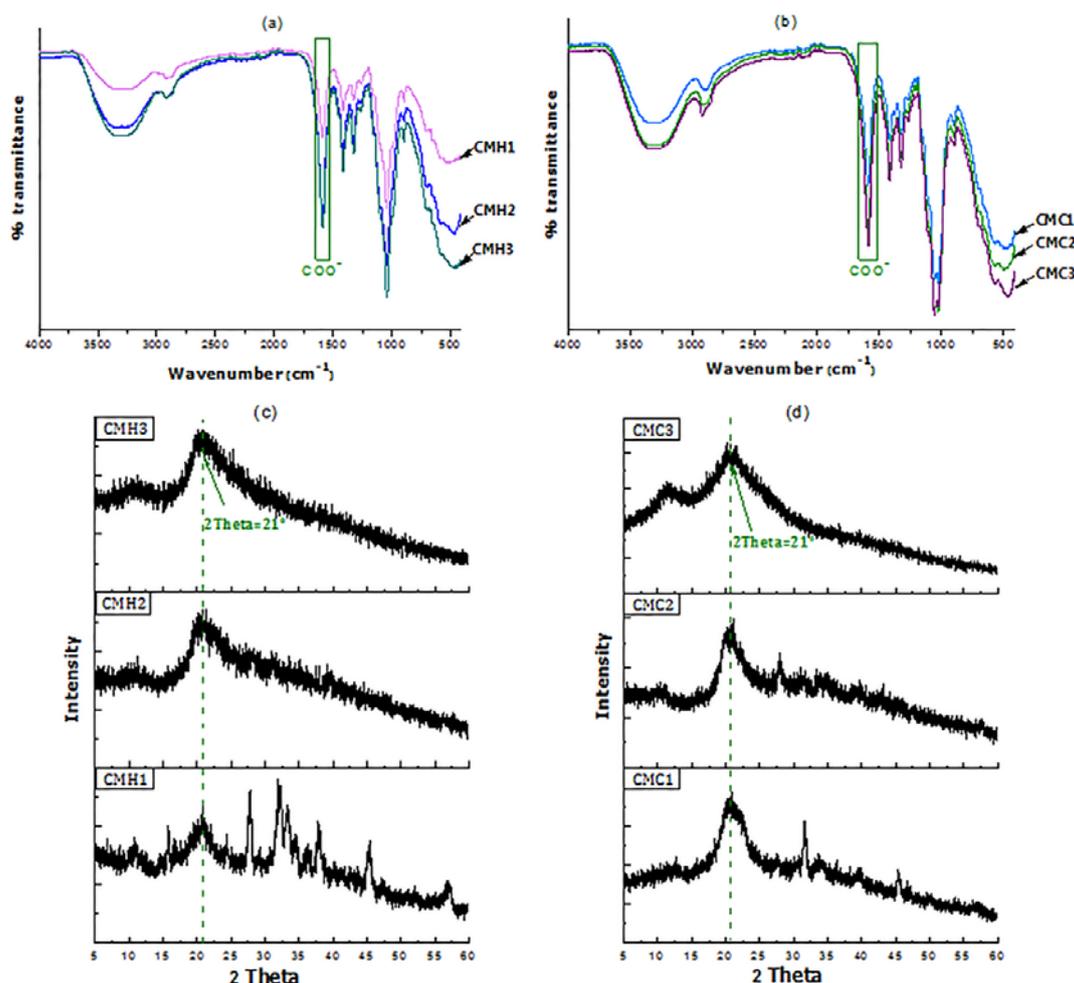


Figure 5: Characterization of carboxymethyl holocellulose by (a) FTIR, (c) XRD, and of carboxymethyl cellulose by (b) FTIR, (d) XRD

Table 3
Main absorption bands in prepared CMH and CMC and their assignment

Wavenumber (cm ⁻¹)		Assignment
CMH	CMC	
3352	3329	O-H stretching
2920	2922	C-H stretching
1595	1595	C=O region (CMC indication)
1410	1412	CH ₂ bonding (CMC indication)
1323	1322	OH in plane bending
1089	1103	C-O-C asymmetry bridge stretching
1042	1052	C-O symmetry stretching alcohol
895	895	β-glycoside linkage

The second weight loss for CMC3 and CMH3 occurred in the temperature range from 180 to 380 °C, and amounted to 37% and 64%, respectively.

In the carboxymethylated samples, this weight loss was due to the decarboxylation of COO⁻ groups in CMC and CMH and thus to the loss of

CO₂. Also, the residue of samples CMC3 and CMH3 was 33.4% and 17.28%, respectively.

SEM analysis

The SEM images of CMCs and CMHs synthesized via carboxymethylation modification of cellulose and holocellulose, with different degrees of substitution, are given in Figure 6. The SEM micrographs of the etherified cellulosic fibers with the lowest DS (CMC1 and CMH1) show a clear change in the surface of cellulose

and holocellulose fibers after the chemical modification; the fiber surface transforms from a relatively smooth surface to a rougher one. This change results from the heterogeneous introduction of the voluminous carboxymethyl groups onto the fiber surface. For those two products, the fiber structure is still present and identifiable, but the more the degree of substitution increases, the more the morphology of the synthesized products changes and the fiber structure no longer exists.

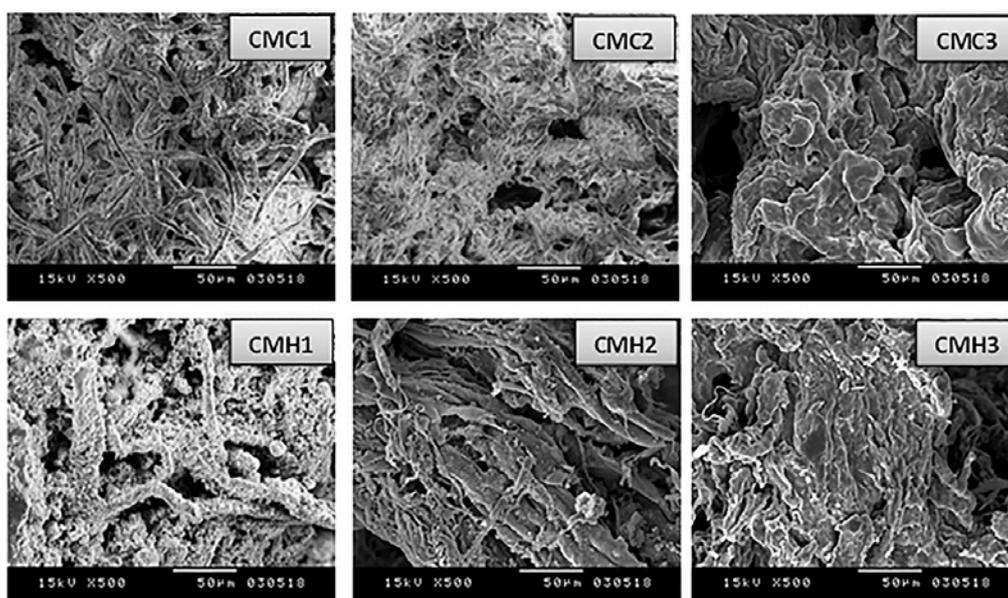


Figure 6: SEM of carboxymethylated cellulose (CMC) and carboxymethylated holocellulose (CMH) obtained with different degrees of substitution

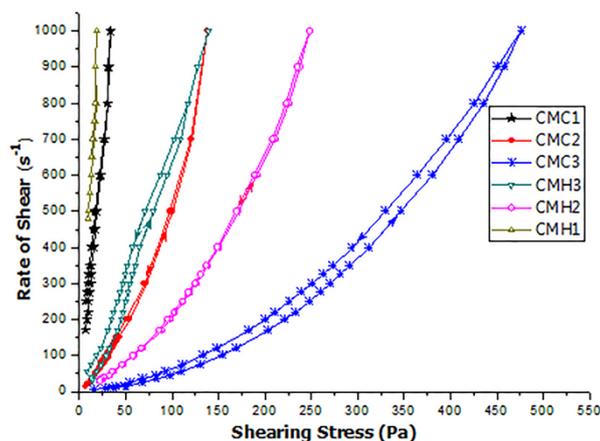


Figure 7: Rheograms of aqueous solutions of prepared CMC and CMH with different degrees of substitution

Table 4
Effect of DS of CMC and CMH on the apparent viscosity at various shear rates

Shear rate (s ⁻¹)	Apparent viscosity (η) in centipoise at room temperature					
	Carboxymethyl cellulose			Carboxymethyl holocellulose		
	DS=0.43	DS=0.88	DS=1.23	DS=0.78	DS=1.04	DS=1.37
170	46.19	274.46	1201	-	520.58	239.08
200	49.53	269.46	1108	-	489.74	224.08
300	46.89	240.38	903.03	-	417.94	182.04
500	43.16	201.42	694.57	18.73	342.96	158.55
700	45.67	174.04	585.02	22.42	300.53	155.52
1000	36.66	138.05	476.93	18.77	248.20	139.54

Rheological properties of prepared CMCs and CMHs

The rheological properties of any material are generally regarded as important parameters to determine its performance and to predict most of its applications. Since the carboxymethyl cellulose is used in many industries in aqueous solutions, it seems interesting to study the viscometric and rheological properties of the carboxymethylated products already synthesized.

The rheograms of aqueous solutions of CMC and CMH are depicted in Figure 7 and the results indicate that all the aforementioned materials present non-Newtonian thixotropic behavior. This reveals the heterogeneity of the molecular structure of the solutions, which are not amenable to regain (rebuilding of structure) the initial state immediately upon removal of the external shear, but after a period of rest.

The effect of the degree of substitution on the apparent viscosity (η) of the aqueous solutions of CMC and CMH was studied and the results were presented in Table 4. It is clear from the data of this table that by increasing the DS of the synthesized carboxymethyl cellulose, the apparent viscosity also increases, and this is true regardless of the shear rate. For example, at a shear rate of 300 s⁻¹, the apparent viscosity increases from 46.89 to 240.38 and to 903.03 centipoise as the DS increases from 0.43 to 0.88 and to 1.23, respectively. However, the apparent viscosity of carboxymethyl holocellulose has a different behavior according to DS. While it can be seen clearly that by increasing the DS from 0.78 to 1.04, the apparent viscosity increases, for a DS equal to 1.37, the viscosity drops obviously and this is probably due to the intra-macromolecular hydrophobic interactions.

CONCLUSION

Tunisian wheat straw is an agricultural by-product available in large quantities and contains

high amounts of holocellulose (72%) and cellulose (41.4%); it therefore has great potential to be used as feedstock for producing carboxymethylated products. Chemical treatment of this biomass with sodium chlorite eliminates lignin, resulting in holocellulose. An alkaline treatment of the holocellulose using potassium hydroxide removes the hemicelluloses and the product obtained consists of cellulose.

The carboxymethylation of the holocellulose and of the cellulose isolated from the biomass was performed under heterogeneous conditions by alkalization using NaOH, followed by etherification with monochloroacetic acid (MCA). The modification reaction converts holocellulose into carboxymethyl holocellulose (CMH), and cellulose into carboxymethyl cellulose (CMC). It has been shown that, by increasing the MCA amount, the extent of the carboxymethylation reaction increases with an increasing degree of substitution (DS).

The chemical structure, crystallinity and morphology of the CMH and CMC samples synthesized were investigated according to the DS. FTIR spectroscopy confirmed the occurrence of the carboxymethylation reaction for all the products by the presence of the signal characteristic of the carboxylate groups. Furthermore, X-ray diffraction demonstrated a decrease in the crystallinity of the carboxymethylated products, compared to the untreated products. Also, the SEM observations showed that the morphological structure was significantly affected by the carboxymethyl content in the sample.

The CMH and CMC obtained from wheat straw are water-soluble, and rheological studies showed that the aqueous solutions of these materials are non-Newtonian, with different degrees of thixotropy. The results from this study reveal that low-cost CMH and CMC can be successfully prepared from wheat straw and that

these ether derivatives are suitable, in accordance with their DS, for a wide range of industrial applications, such as surface sizing in the paper or textile industries, an idea that will be studied and detailed in a further study.

ACKNOWLEDGEMENT: The authors would like to thank Professor Sami Boufi from Faculty of Science-LMSE, University of Sfax, Tunisia, for the technical support regarding TGA analysis.

REFERENCES

- ¹ A. Mtibe, L. Z. Liganiso, A. P. Mathew, K. Oksman, M. J. John *et al.*, *Carbohydr. Polym.*, **118**, 1 (2015), <https://doi.org/10.1016/j.carbpol.2014.10.007>
- ² W. Marzouk, R. Zarrougui and H. Majdoub, *Cellulose Chem. Technol.*, **51**, 621 (2017), [http://www.cellulosechemtechnol.ro/pdf/CCT7-8\(2017\)/p.621-629.pdf](http://www.cellulosechemtechnol.ro/pdf/CCT7-8(2017)/p.621-629.pdf)
- ³ R. Bakker, H. Elbersen, R. Poppens and J. P. Lesschen, Rice straw and Wheat straw. Potential feedstocks for the Biobased Economy, 2013, <https://library.wur.nl/WebQuery/wurpubs/fulltext/288866>
- ⁴ U. Huner, H. A. Gulec and I. Damar Huner, *J. Appl. Polym. Sci.*, **135**, 45828 (2018), <https://doi.org/10.1002/app.45828>
- ⁵ S. Ayadi, Z. Chamekh, C. Karmous, S. Jallouli, N. Ahmed *et al.*, *J. New Sci.*, **15**, 511 (2015), <http://www.jnsiences.org/agri-biotech/23-volume-15.html>
- ⁶ R. Ranieri, *Pastaria Int.*, 2015, http://www.openfields.it/sito/wp-content/uploads/2016/01/PASTARIA2015_N06_en-artOF.pdf
- ⁷ R. Liu, H. Yu and Y. Huang, *Cellulose*, **12**, 25 (2005), <https://doi.org/10.1007/s10570-004-0955-8>
- ⁸ Y. Habibi, *Chem. Soc. Rev.*, **43**, 1519 (2014), <https://doi.org/10.1039/C3CS60204D>
- ⁹ M. Edali, M. N. Esmail and G. H. Vatistas, *J. Appl. Polym. Sci.*, **79**, 1787 (2001), [https://doi.org/10.1002/1097-4628\(20010307\)79:10%3C1787::AID-APP70%3E3.0.CO;2-2](https://doi.org/10.1002/1097-4628(20010307)79:10%3C1787::AID-APP70%3E3.0.CO;2-2)
- ¹⁰ H. Toğrul and N. Arslan, *Carbohydr. Polym.*, **54**, 73 (2003), [https://doi.org/10.1016/S0144-8617\(03\)00147-4](https://doi.org/10.1016/S0144-8617(03)00147-4)
- ¹¹ M. S. Yeasmin and M. I. H. Mondal, *Int. J. Biol. Macromol.*, **80**, 725 (2015), <https://doi.org/10.1016/j.ijbiomac.2015.07.040>
- ¹² A. Ragheb, S. Nassar, I. A. El-Thalouth, M. Ibrahim and A. Shahin, *Carbohydr. Polym.*, **89**, 1044 (2012), <https://doi.org/10.1016/j.carbpol.2012.03.054>
- ¹³ R. Candido and A. Gonçalves, *Carbohydr. Polym.*, **152**, 679 (2016), <https://doi.org/10.1016/j.carbpol.2016.07.071>
- ¹⁴ V. Pushpamalar, S. Langford, M. Ahmad and Y. Lim, *Carbohydr. Polym.*, **64**, 312 (2006), <https://doi.org/10.1016/j.carbpol.2005.12.003>
- ¹⁵ A. Biswas, S. Kim, G. W. Selling and H. Cheng, *Ind. Crop. Prod.*, **60**, 259 (2014), <https://doi.org/10.1016/j.indcrop.2014.06.004>
- ¹⁶ L. E. Wise, M. Murphy and A. A. D'Addieco, *Paper Trade J.*, **122**, 35 (1946).
- ¹⁷ S. Mansouri, R. Khiari, F. Bettaieb, A. El-Gendy and F. Mhenni, *J. Polym. Environ.*, **23**, 190 (2015), <https://doi.org/10.1007/s10924-014-0691-6>
- ¹⁸ A. Thygesen, J. Oddershede, H. Lilholt, A. B. Thomsen and K. Ståhl, *Cellulose*, **12**, 563 (2005), <https://doi.org/10.1007/s10570-005-9001-8>
- ¹⁹ I. Moussa, R. Khiari, A. Moussa, M. F. Mhenni and M. N. Belgacem, *Cellulose Chem. Technol.*, **52**, 841 (2018), [http://www.cellulosechemtechnol.ro/pdf/CCT9-10\(2018\)/p.841-851.pdf](http://www.cellulosechemtechnol.ro/pdf/CCT9-10(2018)/p.841-851.pdf)
- ²⁰ P. Rachtanapun and R. Suriyatem, Project Report, Chiang Mai University, Thailand, 2009, pp. 1-55, <http://www.phtnet.org/download/phtic-research/35.pdf>
- ²¹ J. Batdorf and J. Rossman, in "Industrial Gums: Polysaccharides and Their Derivatives", edited by R. L. Whistler and J. N. BeMiller, Academic Press, New York, 1973, pp. 695-729.
- ²² H. Cheng, M. Takai and E. A. Ekong, *Macromol. Symp.*, **140**, 145 (1999), <https://doi.org/10.1002/masy.19991400116>
- ²³ S. M. Rosa, N. Rehman, M. I. G. de Miranda, S. M. Nachtigall and C. I. Bica, *Carbohydr. Polym.*, **87**, 1131 (2012), <https://doi.org/10.1016/j.carbpol.2011.08.084>
- ²⁴ I. Ghosh, Q. Haider and C. Sharma, *Cellulose Chem. Technol.*, **53**, 643 (2019), <https://doi.org/10.35812/CelluloseChemTechnol.2019.53.63>
- ²⁵ J. I. Morán, V. A. Alvarez, V. P. Cyras and A. Vázquez, *Cellulose*, **15**, 149 (2008), <https://doi.org/10.1007/s10570-007-9145-9>
- ²⁶ B.-J. Lin and W.-H. Chen, *Front. Energ. Res.*, **3**, 2015, <https://doi.org/10.3389/fenrg.2015.00004>
- ²⁷ W.-H. Chen, S.-C. Ye and H.-K. Sheen, *Bioresour. Technol.*, **118**, 195 (2012), <https://doi.org/10.1016/j.biortech.2012.04.101>
- ²⁸ X. Zhou, W. Li, R. Mabon and L. J. Broadbelt, *Energ. Technol.*, **5**, 52 (2017), <https://doi.org/10.1002/ente.201600327>
- ²⁹ R. K. Singh and A. K. Singh, *Waste Biomass Valorif.*, **4**, 129 (2013), <https://doi.org/10.1007/s12649-012-9123-9>
- ³⁰ C. M. Y. Huang, P. X. Chia, C. S. S. Lim, J. Q. Nai, D. Y. Ding *et al.*, *Cellulose Chem. Technol.*, **51**, 665 (2017), [http://www.cellulosechemtechnol.ro/pdf/CCT7-8\(2017\)/p.665-672.pdf](http://www.cellulosechemtechnol.ro/pdf/CCT7-8(2017)/p.665-672.pdf)
- ³¹ M. Yáñez, B. Matsuhiro, S. Maldonado, R. González, J. Luengo *et al.*, *Cellulose*, **25**, 2901 (2018), <https://doi.org/10.1007/s10570-018-1766-7>

³² D. M. dos Santos, A. de Lacerda Bukzem, D. P. R. Ascheri, R. Signini and G. L. B. de Aquino, *Carbohydr. Polym.*, **131**, 125 (2015), <https://doi.org/10.1016/j.carbpol.2015.05.051>

³³ M. Akram, I. Taha and M. M. Ghobashy, *Cellulose*, **23**, 1713 (2016), <https://doi.org/10.1007/s10570-016-0950-x>

³⁴ E. A. Hassan, M. L. Hassan, C. N. Moorefield and G. R. Newkome, *Carbohydr. Polym.*, **116**, 2 (2015), <https://doi.org/10.1016/j.carbpol.2014.06.056>

³⁵ R. Khiari, M. F. Mhenni, M. N. Belgacem and E. Mauret, *Bioresour. Technol.*, **101**, 775 (2010), <https://doi.org/10.1016/j.biortech.2009.08.079>