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Homogeneous microwave-assisted carboxymethylation from totally chlorine free bleached olive tree pruning residues pulp

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Abstract: This study deals with a new methodology for the production of carboxymethyl cellulose (CMC) from olive pruning residues, agricultural by-products. Cellulose was extracted by the soda–anthraquinone pulping process, and the pulp bleaching was performed using totally chlorine free (TCF) bleaching. Then, CMC microwave-assisted synthesis was performed in a homogeneous media, using DMA/LiCl as a cellulose solvent. A Box–Behnken design was applied in order to evaluate which parameters of the carboxymethylation process (*viz*. reaction time, reaction temperature, and amount of monochloroacetic acid) affect the degree of substitution and the yield of the synthesis reaction of this cellulose derivative. Optimized conditions to yield CMC were determined based on the desirability function approach. The prepared materials under synthesis using the optimal conditions were characterized using several analytical tools, *i.e.*, FTIR, TGA, DSC and SEM. This cellulose derivative was successfully fabricated by a fast and efficient microwave-assisted method and thus would provide many opportunities for diverse applications.

Keywords: agricultural by-product; cellulose; pulping; carboxymethyl cellulose synthesis.

INTRODUCTION

Cellulose is the principal constituent of all plant cell walls. It is the most abundant and important biopolymer on earth, almost inexhaustible, renewable material, and environmentally benign. It still possesses high potential for future applications; it can be easily modified to more natural and sustainable alter-

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natives compared to synthetic products. The main raw material of cellulose derivative is cellulose from wood pulp (containing 40–50 % cellulose) and cotton linters (contain 90 % cellulose). However, nowadays uses of these raw materials of cellulose resources are discouraged because of the cost of production and increasing environmental concerns.[1,2] The attention is focused on the recovery of waste ("waste-to-value").

The global agriculture sector produces annually billions of tons of agricultural biomass. However, this progress has also led to the generation and accumulation of agricultural wastes of little commercial value. Only a small fraction of agricultural wastes are used, as animal feeds and for energy production.[3] In particular, pruning of olive trees generates a large amount of biomass that is burned, causing severe environmental concern, or left in farmland as a source of food for animals. Therefore, the transformation of this agricultural residue into value-added products is interesting. Note that according to estimates from many countries, 25 kg of leaves and twigs are produced per year per tree.[4]

Moreover, carboxymethyl cellulose (CMC) is one of the most important water-soluble derivatives of cellulose. It is available in several grades (technical, semi-purified, purified, and extra purified) and it is widely employed in many areas of industry and human life, such as detergents, paper coating, textile sizing and printing, ceramic, food, toothpaste, pharmaceuticals, *etc.*[5] It is formed by the carboxymethylation of the hydroxyl group in cellulose.[6] In this context, the valorization of olive pruning residues, a widely available agriculture by-product in Tunisia, was realized by the synthesis of CMC. Indeed, as raw materials for CMC synthesis, cleaned and crushed olive tree pruning residues was delignified using the soda–anthraquinone pulping process. Then, the obtained pulp was bleached using totally chlorine-free bleaching sequences (TCF), the most environmentally bleaching process that uses only oxygen-based bleaching chemicals.

The commercial production of carboxymethyl cellulose (CMC) is carried out by using a heterogeneous slurry of cellulose in a solvent that swells but neither dissolves the starting polymer nor the CMC obtained. Under these reaction conditions, the CMCs thus obtained have a non-uniform distribution of substituents within the anhydroglucose unit. On the other hand, homogeneous carboxymethylation reactions offer reaction uniformity and should produce a more even distribution of substituents than heterogeneous processes.[7]

As known, cellulose is a homopolysaccharide that is formed from linearly connecting D-glucose units condensed through $\beta(1-4)$ glycosidic bonds. It possesses a highly crystalline structure due to the presence of extensive intra- and intermolecular hydrogen bonding. Consequently, this natural polymer is insoluble in water and typical organic solvents and can only be dissolved if the intra- and intermolecular hydrogen bonds are effectively disrupted.[8] Thus, the dissolution of cellulose destroys the highly organized hydrogen-bonding system surrounding the polyglucan chain. Salt systems in non-aqueous solvents are widely used to dissolve cellulose.[9] Here, the dissolution of the obtained bleached pulp was carried out, using LiCl/DMAc (lithium chloride in *N*,*N*-dimethylacetamide). It is a non-derivatizing solvent, *i.e.*, one that causes dissolution without forming covalent bonds. This step was followed by a reaction with a derivatizing agent (monochloroacetic acid (MCA)) to obtain the desired product (CMC).

By combining major green chemistry principles, *viz.*, the use of renewable biomass materials and the choice of a rapid method allows a high value-added application of biomass. Indeed, herein a fast microwave-assisted method for CMC synthesis is reported. In recent years, microwave chemistry has become increasingly popular within organic synthesis.[10,11] Compared with conventional heating, microwave-assisted heating, under controlled conditions, is an advanced technology in reducing reaction time besides increasing product yield and purity.[12–14] Microwave irradiation–assisted synthesis has been widely used in the chemical functionalization of polymer materials. It has been developed for cellulose modification processes including acetylation[15] and carboxymethylation.[16] Therefore, microwave irradiation is a promising method to modify the physicochemical properties of cellulose.

Herein, an attempt was made to exploit a lignocellulosic material widely available in Tunisia as a source of cellulose fibers to develop a new microwave-assisted method for preparing CMC from totally chlorine free-bleached pulp in a homogeneous media using LiCl/*N*,*N*-dimethylacetamide as a solvent. The optimal conditions for unconventional CMC preparation were predicted by the response surface regression model, and the CMC product was characterized.

EXPERIMENTAL

Raw materials

The olive tree pruning residues used in this work were collected from the province of Monastir-Tunisia. Leaves and stems were separated in order to study each material separately. Cleaned and crushed raw materials were then used for cellulose extraction.

Pulping procedure

Soda–anthraquinone pulping experiments were performed in a rotating system and heated under controlled temperature. The following cooking conditions were employed: liquor ratio was 10:1, temperature 140 °C for leaves and 110 °C for stems, and cooking time of 1 h for leaves and 3 h for stems. The alkali charge was 8 mass % for leaves and 16 mass % for stems with freshly prepared caustic soda, and the amount of anthraquinone was 0.1 mass % based on the oven-dry weight of the raw materials. After cooking, the pulp obtained through filtration was extensively washed with water until free of residue alkali. The pulp yield was determined after oven drying to constant weight.

Bleaching procedure

The obtained pulp was bleached by TCF (totally chlorine free) bleaching processes, using only a peroxide that has the role to eliminate chromophores in the lignin structures. It was selected due to its least hazardous and oxidative damaging potential. Thus, pulp bleaching was carried out by a simple stage peroxide sequence QP (where Q-chelating treatment and P-hydrogen peroxide bleaching stage). The following chelating stage (Q) conditions were employed: 10 % consistency, 0.25 % EDTA during 2 h at 70 °C in a slightly acidic medium (pH regulation by H_2SO_4). Then, the last peroxide stage (P) conditions were employed: 10 % consistency, 0.2 % EDTA, 0.2 % $MgSO_4$ during 3 h (1 h) at 90 °C (75 °C) with 2.25 % of H_2O_2 (5 %) for olive stems (respectively for olive leaves). The final brightness of 84 was attained for both pulps, leaves, and stems.

Carboxymethylation of cellulose in DMAc LiCl medium

The microwave-assisted synthesis of CMCs under homogeneous reaction conditions of the obtained bleached pulps was carried out in two steps, *i.e.*, cellulose dissolution and etherification. For cellulose dissolution, DMAc/LiCl was selected as a non-derivatizing solvent, *i.e.*, one that causes dissolution without forming covalent bonds. This step was followed by a reaction with a derivatizing agent (monochloroacetic acid (MCA)) to obtain the desired product (CMC). Thus, the oven-dried bleached pulp of cellulose (0.1 g) was kept at 130 °C under magnetic stirring in 6 ml of *N*,*N*-dimethylacetamide (DMAc) for 2 h. After cooling to 100 °C, 0.3 g of anhydrous LiCl was added to the slurry. Then the slurry was cooled down to room temperature under stirring and left standing overnight. The next day, a suspension of the desired amount of MCA in 2 ml of DMAc was added and stirred for 10 min at room temperature, followed by a suspension of NaOH 40% (2 ml) in 2 ml DMAc. Afterwards, microwave irradiation in a monomode microwave reactor (CEM discover automated reactor) was applied on the suspension with stirring under pressure according to the conditions of the experimental plan presented in Table I. Finally, the reaction mixture was precipitated into 30 ml of ethanol. After filtration, the solid product obtained as CMC was washed extensively with ethanol to remove undesirable by-products and dried at 50 °C.

TABLE I. Box–Behnken experimental design (BBD) for the carboxymethylation process

Run order	Factors			Responses			
	τ / min	t / °C	Amount of MCA,	Olive leaves		Olive stems	
	(X_1)	(X_2)	g per g of cellulose (X_3)	DS[a]	Yield[b], %	DS[a]	Yield[b], %
1	5 (–1)	70 (–1)	4.5 (0)	0.87	157.21	0.95	160.63
2	15 (1)	70 (–1)	4.5 (0)	0.63	150.88	0.64	154.62
3	5 (–1)	90 (1)	4.5 (0)	0.74	152.11	0.68	155.66
4	15 (1)	90 (1)	4.5 (0)	1.32	174.87	1.39	177.21
5	5 (–1)	80 (0)	3 (–1)	0.42	146.14	0.47	149.74
6	15 (1)	80 (0)	3 (–1)	0.98	158.32	1.03	162.23
7	5 (–1)	80 (0)	6 (1)	1.18	168.81	1.25	171.14
8	15 (1)	80 (0)	6 (1)	1.68	192.48	1.87	196.27
9	10 (0)	70 (–1)	3 (–1)	0.81	155.04	0.83	159.24
10	10 (0)	90 (1)	3 (–1)	1.36	176.24	1.47	177.96
11	10 (0)	70 (–1)	6 (1)	1.44	180.02	1.55	182.22
12	10 (0)	90 (1)	6 (1)	1.15	166.13	1.22	170.08
13	10 (0)	80 (0)	4.5 (0)	1.43	179.34	1.55	182.14
14	10 (0)	80 (0)	4.5 (0)	1.42	177.95	1.57	181.01
15	10 (0)	80 (0)	4.5 (0)	1.41	178.4	1.55	181.42

[a]Degree of substitution of carboxymethyl groups; [b]yield of carboxymethylation

Experimental design and statistical analysis

A Box–Behnken response surface design was used to analyze the main effects and interactions of the variables (*viz.*, time, temperature of the microwave irradiation, and the amount of monochloroacetic acid (MCA) per g of cellulose) in the response variables average, degree of substitution (DS), and reaction yield.

As this design is suitable for the exploration of quadratic response surfaces and constructs a second-order polynomial model,[17] it was used to optimize the conditions for CMC microwave-assisted synthesis from olive tree pruning residue from a small number of experimental runs.

Fifteen experiment runs were performed with different combinations of three factors with three replicates at the center point to estimate the pure error. For each run, the experimental responses are shown in Table I.

Characterization

The prepared materials thus synthesized under optimal conditions were then characterized.

Determination of the degree of substitution of carboxymethyl groups. In this work, to determine the DS of the prepared CMC samples, a titration method was used. This technique is widely described in the literature.[18] Firstly, the sample was mineralized at 600 °C for 4 h. Before the titration, the obtained ash which contained Na_2O was dissolved in hot water at 80 °C. Next, the solution was titrated with 0.1 N (0.05 M) H_2SO_4 in the presence of Methyl Orange as the titration indicator. The reddish solution thus obtained was subsequently heated to remove dissolved CO_2 until it became yellow. So, a ratio *B* can be defined, and the *DS* estimated using:[18]

$$B = \frac{0.1V}{m_{\mathrm{CMC}}} \tag{1}$$

where 0.1 is the normality of the sulfuric acid solution, *V* is the total volume of the titrating solution added to neutralize the ash solution, and m_{CMC} is the oven-dried weight of the initial sample and:

$$DS = \frac{0.162B}{1-0.08B} \tag{2}$$

where 0.162 and 0.08 are, respectively, the molar masses ($\mathrm{kg \cdot mol^{-1}}$) of the glucose units and $CHCOO^{-}Na^{+}$ groups substituted on the cellulose.

These measurements were duplicated and the difference between the two values was within an experimental error of 5 %.

The yield of carboxymethylation. The yield of carboxymethylation reaction was measured on a dry basis by dividing the dry weight of carboxymethyl cellulose (m_{CMC}) by the dry weight of the bleached pulp of olive tree branch cellulose ($m_{\mathrm{cellulose}}$), as shown:

$$\mathrm{Yield} = 100\frac{m_{\mathrm{CMC}}}{m_{\mathrm{cellulose}}} \tag{3}$$

Scanning electron microscopy (SEM). The morphological variations were studied using a high-resolution SEM instrument. The dry sample was spread on a double-sided conducting adhesive tape, pasted on a metallic stub, coated with gold in an anion sputter coating unit for 2 min, and observed in a JEOL-JSM-IT100 electron probe micro-analyzer at 15 kV.

FTIR studies. FTIR spectra were used to characterize the samples, which were recorded with an FTIR-8400S Shimadzu Fourier transform infrared spectrophotometer, at room temperature in the range of 4000–500 cm^{-1}.

Thermogravimetric analysis (TGA). Thermal stabilities of samples were recorded using TGA Q500 V20.10 Build 36 instrument to measure the weight loss at different temperatures with a heating range 35 to 800 °C at a rate of 10 °C min^{-1}.

Differential scanning calorimetric analysis (DSC). The thermal behavior of CMC was studied using DSC Q200 V24.4 Build 116 thermal analyzer. The sample was inserted into the aluminum pan and a DSC scan was first made from 25 to 180 °C at a heating rate of 10 min^{-1} under nitrogen atmosphere at a flow rate of 50 mL. Then it was cooled to clear the thermal history of the sample. The second scan is then carried out from 25 to 250 °C at a speed of 10 °C min^{-1}. The results were recorded and analyzed.

RESULTS AND DISCUSSION

Statistical analysis and the optimization of carboxymethylation conditions

Regression analysis presented in Table II indicates that the model equations can adequately be used to describe the microwave-assisted CMC synthesis under a wide range of operating conditions. The coefficient of determination (R^2) is a measure of the degree of fit and a good model fit should yield an R^2 of at least 0.8.[19,20] This means that the response model evaluated in this study can explain very well the CMC microwave-assisted synthesis for the two studied raw materials, olive tree leaves and olive tree stems.

TABLE II. Regression analysis of a full second-order polynomial model for optimization of microwave-assisted synthesis of CMCs

Terms	Olive leaves				Olive stems			
	DS[a]		Yield[b], %		*DS*[a]		Yield[b], %	
	Coeff[c]	*p*[d]	*Coeff*[c]	*p*[d]	*Coeff*[c]	*p*[d]	*Coeff*[c]	*p*[d]
Constant	1.420	0.000	178.56	0.000	1.557	0.000	181.52	0.000
X_1	0.175	0.061	6.53	0.058	0.197	0.053	6.65	0.054
X_2	0.102	0.218	3.28	0.274	0.098	0.263	3.03	0.305
X_3	0.235	0.023	8.96	0.020	0.261	0.021	8.82	0.021
$X_1\times \mathrm{X}_1$	–0.327	0.028	–11.36	0.034	-0.377	0.022	-11.01	0.037
$X_2\times X_2$	–0.202	0.117	–8.44	0.085	-0.265	0.070	-8.48	0.081
$X_3\times X_3$	–0.027	0.807	–0.77	0.853	-0.025	0.840	-0.67	0.871
$X_1\times X_2$	0.205	0.103	7.27	0.112	0.255	0.070	6.89	0.125
$X_1\times X_3$	–0.015	0.890	2.87	0.481	0.015	0.898	3.16	0.437
$X_2\times X_3$	–0.210	0.097	–8.77	0.068	-0.242	0.080	-7.71	0.094
R^2	88.51		89.03		89.83		88.62	

[a] Degree of substitution of carboxymethyl groups; [b] yield of carboxymethylation; [c] regression coefficients; [d] *p*-value used to measure the significance of each parameter

The *p*-value was used as a tool to check the significance of each parameter. A value lower than 0.05 indicates that the term is statistically significant, whereas a value higher than 0.10 indicates that the term is not significant. Regarding the responses of DS and yields for the two raw materials thus studied, the time of microwave irradiations (X_1) was a significant parameter as *p*-value was less than 0.05 and the amount of MCA (X_3) was slightly significant because the p-value was less than 0.1. Whereas the temperature (X_2) was not a significant factor since the *p*-value was more than 0.1. By applying response surface methodology, the predictive equations for homogeneous microwaves assisted synthesis of CMC without the non-significant terms and in uncoded units were expressed as follows:

For olive tree leaves:

$$DS = 1.420 + 0.175X_1 + 0.235X_3 - 0.327X_1^2 - 0\ .210X_2X_3 \quad (4)$$

$$Y = 178.56 + 6.53X_1 + 8.96X_3 - 11.36X_1^2 - 8.44X_2^2 - 8.77X_2X_3 \quad (5)$$

For olive tree stems:

$$DS = 1.557 + 0{,}1975X_1 + 0.2612X_3 - 0.377X_1^2 \text{ -}0.265X_2^2 + \\ + 0.255X_1X_2 - 0.242X_2X_3 \quad (6)$$

$$Y = 181.52 + 6.65X_1 + 8.82X_3 - 11.01X_1^2 - 8.48X_2^2 - 7.71X_2X_3 \quad (7)$$

Optimization of carboxymethylation conditions

The optimal process parameters were found by using optimization choice in Minitab software to maximize the responses yield and *DS* which were listed in Table III. The composite desirability index calculated were 0.95 and 0.94 for olive tree leaves and olive tree stems respectively, so highly desirable. To verify the suitability of these predicted optimal values, additional experiments were performed. Experimental results obtained under the same conditions were in agreement with the predicted results, with differences smaller than 5 %.

TABLE III. Predicted optimum values and experimental results in optimum conditions for the microwave-assisted synthesis of CMCs; * – value of mean deviation

Origin	Variables		Yield[a], %		*DS*[b]	
			Predicted	Experimental	Predicted	Experimental
Leaves	τ / min	11	188.83	193.17 ± 0.12*	1.65	1.69 ± 0.0.71*
	t / °C	80				
	Amount of MCA, g per g of cellulose	6				
Stems	τ / min	11	191.85	195.73 ± 0.18*	1.82	1.86 ± 0.94*
	t / °C	80				
	Amount of MCA, g per g of cellulose	6				

[a]Yield of carboxymethylation; [b]degree of substitution of carboxymethyl groups

Morphological analysis by SEM

The SEM micrographs of olive tree raw materials (leaves and stems), celluloses (bleached and unbleached), and CMCs produced by homogeneous microwave-assisted synthesis are presented in Fig. 1.

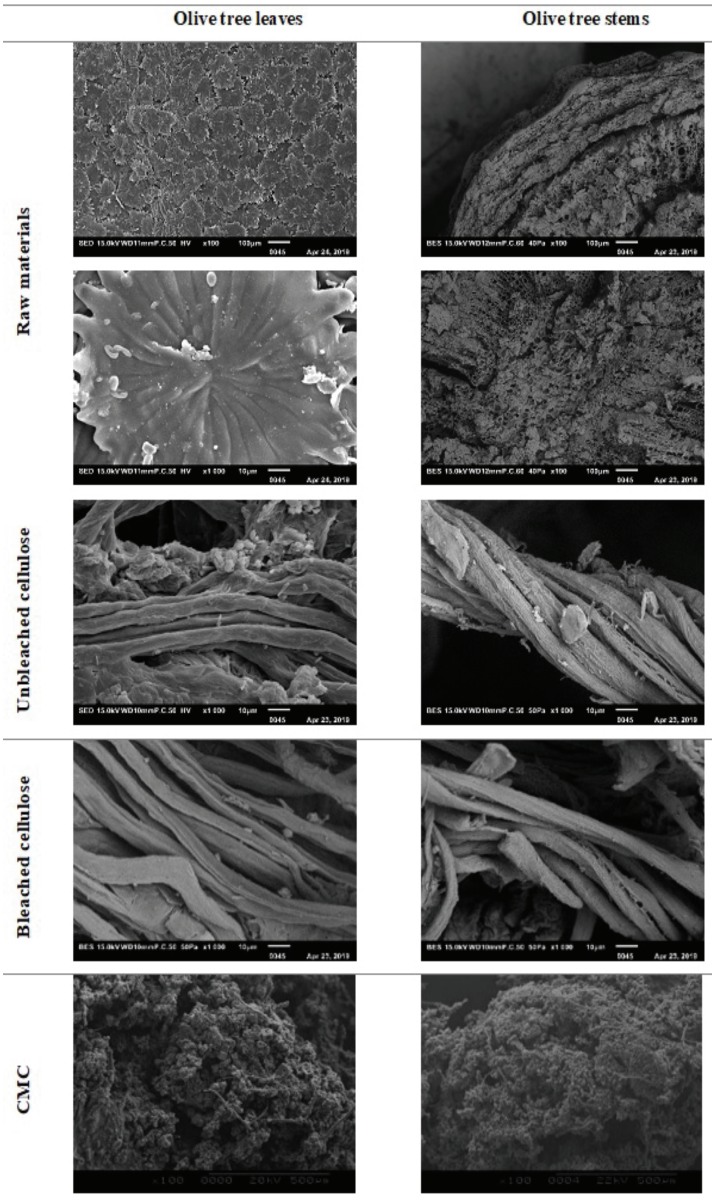

Fig. 1. SEM micrographs of olive tree raw materials (leaves and stems), celluloses, and CMCs produced by homogeneous microwave-assisted synthesis.

The olive tree is an evergreen tree that has foliage throughout the year. As shown in Fig. 1, its leaves are composed of an organized layer of star-shaped cells densely distributed, called trichomes. For stems, the observation of a cross-section shows a multicellular structure and several porous fibers. In fact, it is well recognized that the cellulose chains of natural fibers are linked by lignin and hemicellulose, forming multicellular fibers.

After the soda-anthraquinone delignification process, cellulose was isolated, giving individual fibers while some others remain quite compact because of the amount of residual lignin not removed which hangs up. During the bleaching process, the amount of residual lignin decreases further and fibers become more individualized.

The SEM micrographs of various CMCs powdered samples revealed that the dissolution of the cellulose was successfully carried out, except for a few fibers.

FTIR

After various treatments, FTIR spectroscopy presents an appropriate tool to specify the variations on the chemical structure of the resulting samples. The infrared spectra of bleached celluloses isolated from olive tree leaves and stems as well as different synthesized CMCs are shown in Fig. 2.

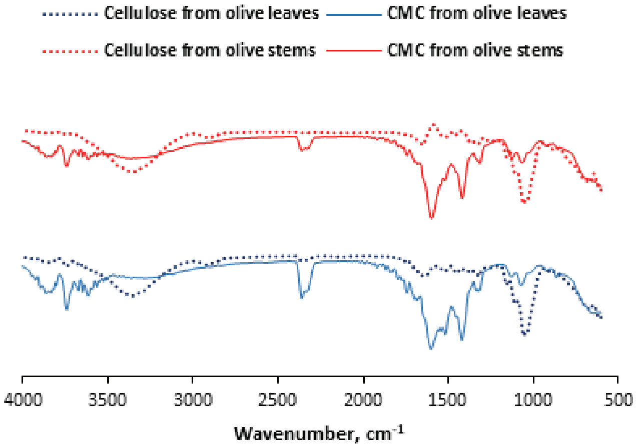

Fig. 2. FTIR spectra of bleached celluloses and CMCs samples prepared from olive tree leaves and olive tree stems.

For both bleached celluloses, as shown in Fig 2, the peaks around 3341 cm^{-1} correspond to the O–H stretching vibration of the –OH groups in cellulose molecules.[21–23] Moreover, the other strong peaks observed at 1034 and 1057 cm^{-1} can be attributed to the C–O–C glycosidic ring skeletal vibration.[24,25]

In the case of all carboxymethylated derivatives thus synthesized, the appearance of an intense absorption band around 1620 cm^{-1} confirms the presence of the carboxylate group (–COO^{-}Na^{+}). Thereby giving evidence that during the modification process hydroxyl groups of cellulose are replaced with carboxyl groups. The absorption bands at 1318 and 1420 cm^{-1} are attributed respectively to the COO stretching in CO_2H and binding in OCH_2.[26]

Thermogravimetric analysis (TGA)

The thermal decomposition of different samples, cellulose and carboxymethyl cellulose (CMC), prepared from olive stems and olive leaves were studied under a nitrogen atmosphere. Their thermogravimetric analysis (TGA) curves are shown in Fig. 3 and their mass losses were evaluated and listed in Table IV.

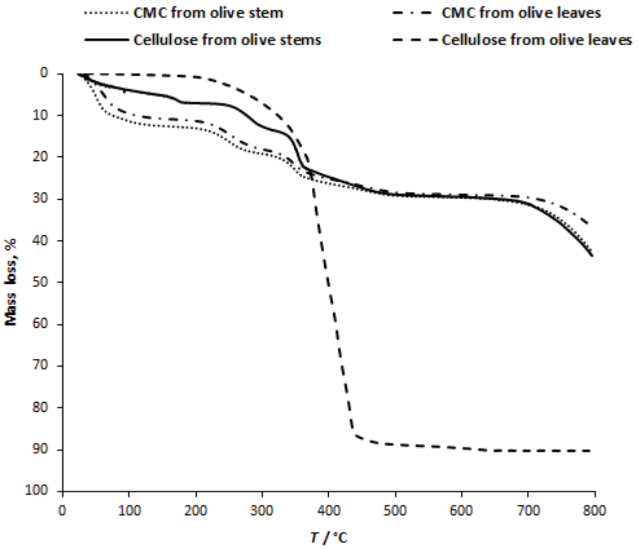

Fig.3. TGA curves of the bleached celluloses and CMCs samples prepared from olive tree leaves and stems.

For the cellulose samples, the onset temperatures are respectively 278 °C for cellulose olive leaves and 141 °C for cellulose from olive stems. Concerning the temperatures of maximum mass loss, a shift of 28 °C was observed between the two samples. According to Zickler *et al.*,[27] cellulose was hardly degraded at temperatures below 310 °C, whereas the kinetics became too fast above 360 °C and the thermal degradation mechanisms differed along and across the cellulose fibrils. A highest weight loss at temperatures higher than 380–400 °C and a sharply lower residual mass after the decomposition step was observed for cellulose from olive leaves (56.45 for cellulose from olive stems *vs.* 9.65 for cellulose from olive leaves). It was observe that the residual mass of cellulose from olive leaves was very low; this indicates their high purity and absence of inorganic residues.

It is well known that the thermal behavior of cellulose can be influenced by its physical properties. So, these results are probably due to the difference in crystallinity, degree of polymerization, and moisture contents.[28] Additionally, these differences might be attributed to the presence of different amounts of residual lignin in the two celluloses after extraction. Whereas, smaller differences appear between the two carboxymethylcelluloses (CMC) samples.

TABLE IV. TGA/DTA thermal parameters for the degradation of different samples prepared from olive tree leaves and stems.

Sample	$t_{5\%}$[a] °C	t_{max}[b] °C	Mass loss at t_{max}, %	Total mass loss, %	Residue %
Cellulose from olive stems	141	352	18.6	43.55	56.45
Cellulose from olive leaves	278	380	32	90.35	9.65
CMC from olive stems	48	355	24	42.7	57.3
CMC from olive leaves	60	353	21	36.9	63.1

[a]Onset temperature; [b]temperature of maximum degradation rate

The thermogravimetric analysis (TGA) and the first derivative thermogravimetric (DTG) curves for the two CMCs studied in a nitrogen atmosphere are shown in Fig. 4.

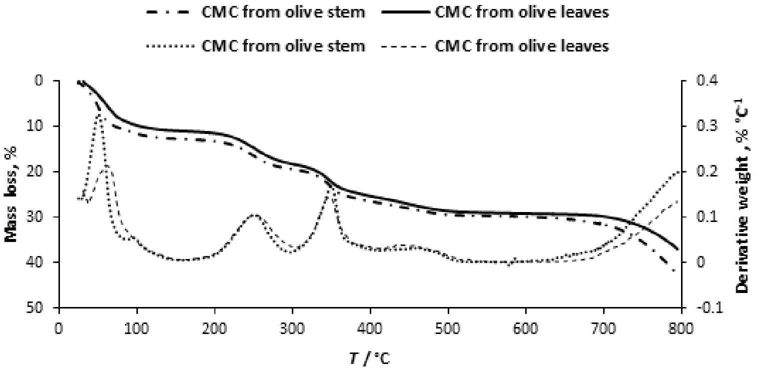

Fig. 4. TGA and DTA curves of the CMCs samples prepared from olive tree leaves and stems.

They have almost the same pace of thermal decomposition. In fact, within 100 °C, weight reduction can be due to moisture loss. The onset temperature ($t_{5\%}$) of both obtained CMC were respectively 48 °C for CMC from olive stems and 60 °C for CMC from olive leaves. At around 353 °C, the residual weight was about 75 %. Beyond 350 °C, the rate of mass loss decreased, revealing the appearance of another pyrolysis mechanism. Increasing temperature more than 700 °C, losing weight proceeded at a slower rate. When the temperature reached 800 °C, the residual mass was about 63 % for CMC obtained from olive tree leaves and 57 % for CMC from olive tree stems. From where complete decomposition of CMC did not occur.

Differential scanning calorimetric analysis (DSC)

Usually, DSC allows the determination of first- and second-order thermal transitions, such as melting, crystallization, and glass transition phenomena.[29] The glass transition temperature, as a second-order transition, is often observed in polymeric systems and is considered as the change between the glassy and rubbery state.

As mentioned above, two heating scans were carried out on each sample. The heating runs of CMCs samples up to 250 °C are shown in Figs. 5 and 6.

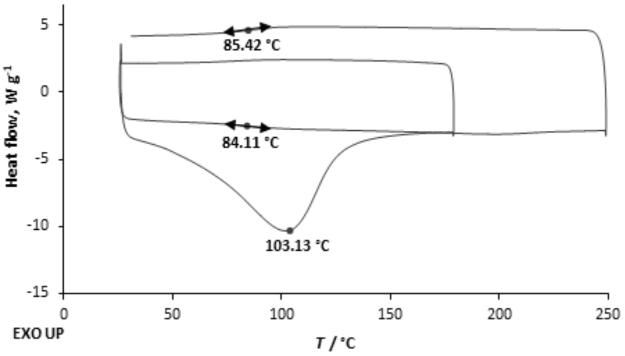

Fig. 5. DSC thermogram of carboxymethyl cellulose prepared from olive tree leaves.

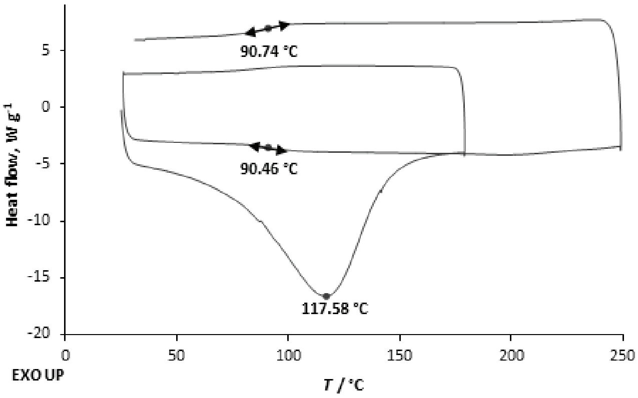

Fig. 6. DSC thermogram of carboxymethyl cellulose prepared from olive tree stems.

The DSC thermograms in the first scan exhibit a sharp peak at around 117 and 103 °C for olive tree stems and olive tree leaves, respectively, which are not apparent in the second scan. Thereby, they might be assigned to the dehydration of cellulose. Then, enthalpy changes were observed in the second scan at around 85 and 90 °C for the samples from olives leaves and olive stems, respectively. These enthalpy changes have obviously been attributed to the glass transition temperatures. In addition, no exothermic peak appeared in the thermograms, which implies that the melting temperature of the CMCs samples would be greater than 250 °C.

CONCLUSIONS

The present work shows that celluloses extracted from olive pruning residues leaves and stems, which were totally chlorine-free bleached, were suitable for the production of carboxymethyl cellulose. The results obtained suggest that it is an agriculture by-product with great potential to be a feedstock for producing this derivative.

Moreover in this work, the development and the optimization of a new methodology for homogeneous carboxymethylation using DMA/LiCl as a cellulose solvent system in a monomode microwave reactor was successfully achieved.

According to surface methodology Box–Behnken design, several reaction conditions were tested to be optimized and different average degrees of substitution were thus obtained. Applying the optimized set conditions: 6 g of monochloroacetic acid per g of cellulose; reaction time of 11 min and temperature of 80 °C, CMCs having a DS of 1.69 and 1.86 can be prepared from olive leaves and stems, respectively. The obtained CMCs were characterized using different tools. The formation of the carboxymethyl group was confirmed by FT-IR spectroscopy. SEM images confirmed that the prepared CMC has a powdered aspect and the dissolution of the cellulosic structure was done successfully.

The obtained results can be considered promising. A highly substituted carboxymethyl cellulose was obtained by a new production process, suitable for use in several fields of application, such as a yarn sizing agent in textile industries.

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ИЗВОД

МИКРОТАЛАСНО ПОТПОМОГНУТА ХОМОГЕНА КАРБОКСИМЕТИЛАЦИЈА ИЗБЕЉЕНИХ ОСТАТАКА ЦЕЛУЛОЗЕ ИЗ ОСТАТАКА ОРЕЗИВАЊА МАСЛИНА ПОСТУПКОМ БЕЗ УПОТРЕБЕ ХЛОРА

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Ова студија се бави новом методологијом за производњу карбоксиметил-целулозе (CMC) из остатака орезивања маслина, нуспроизвода из пољопривреде. Целулоза је екстрахована поступком пулповања сода-антрахиноном, а избељивање пулпе је изведено без хлора (TCF). Затим је изведена микроталасно потпомогнута синтеза CMC у хомогеном медијуму, користећи DMA/LiCl као растварач за целулозу. Примењен је *Box–Behnken* дизајн како би се проценило који параметри процеса карбоксиметилације (односно време реакције, температура реакције и количина монохлорсирћетне киселине) утичу на степен супституције и принос реакције синтезе овог деривата целулозе. Оптимизовани услови за добијање CMC одређени су на приступом функције пожељности. Синтеза припремљених материјала под оптималним условима окарактерисана је употребом неколико аналитичких техника као што су FTIR, TGA, DSC и SEM. Овај дериват целулозе успешно је произведен брзом и ефикасном методом потпомогнутом микроталасном пећницом, што ће пружити бројне могућности за различите примене.

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