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ORIGINAL ARTICLE

Cellulose acetate from biomass waste of olive industry

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Abstract In the present work cellulose powder was extracted from olive industry solid waste and then converted into cellulose acetate. The cellulose powder was extracted from olive industry solid waste by kraft pulping process and multistep bleaching p sequences. An elemental chlorine-free chemical bleaching sequence chlorine dioxide (D)-cold caustic extraction (E)-hypochlorite (H)-hydrogen peroxide (P) was used. Cellulose powder was obtained in about 35 % yield. The extracted cellulose and cellulose acetate made from thereof were extensively characterized using Fourier transform infrared spectroscopy, electron microscopy sciences, gel-permeation chromatography/high-performance liquid chromatography, and viscometry. Our key finding in this study was that olive industry solid waste is a valuable source of cellulose powder and its derivatives. This is important, since our results show how lignocellulosic agricultural wastes could be utilized and converted into cellulose products with high value.

Keywords Olive waste · Kraft pulping · Cellulose acetate · ECF bleaching

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Introduction

The olive oil industry represents one of the most economically important agro-food sectors in the Mediterranean and Middle Eastern regions. For example, according to the Palestinian Ministry of Agriculture, West Bank and Jordan produce approximately, 135 thousand metric tons of olive every year. The size and magnitude of the olive production worldwide means that huge amounts of unexploited agronomic wastes are generated [1], thus posing acute environmental problems in the region.

In general, olive mill waste consists of about 44 % of olive industry solid wastes (OISW) and 56 % of olive industry liquid waste (OILW) [2]. These wastes are acidic, have extremely high biological oxygen demand (BOD) and chemical oxygen demand (COD) values, and also contain toxic levels of polyphenols [1]. The waste materials pose a challenge to the olive mills and a concern to environmentalists, for it presents a serious disposal problem for waste management [1]. In certain countries, the OISW is usually burned or left to rot, thus releasing CO_2 into the atmosphere, while OILW tends to be disposed of via the sewage system, which has implications for water quality. So, waste is one of the major problems faced by industrialists in view of increasing environmental standards by the day. In addition, the olive industry loses economic value by disposing the effluent or selling it for a low price.

The challenge is to utilize and convert these waste materials into useful and low-cost marketable products. Published studies have shown that the olive mill solid waste might be mixed with polypropylene and used as filler in the manufacture of wood-plastic composites [3] or mixed with pure wood fiber for the manufacture of fiber board [2]. Also, waste may be utilized as a soil amendment [4–10], a wetting agent [11], an energy source [12–14], a

biosorbent for heavy metals [15], or treatment to reduce phytotoxicity [16]. There remains a challenge, however, to find an environmentally friendly and economical means of converting OISW into commercial cellulose derivatives. Among all cellulose derivatives, cellulose acetate has been recognized by far as the most important derivative of cellulose due to its extensive industrial and commercial applications [17–20]. There are numerous publications and patents on the preparation and utilization of cellulose acetate. However, to the best of our knowledge there are no known reports addressing the utilization of OISW to prepare cellulose esters. Wood pulp and cotton linters are the major resources for all cellulose derivatives, such as cellulose esters [19], and ethers [20]. Cellulose acetate has been widely used in textile, raw materials in the fields of lacquer, plastics, filter tow [21], films, membranes [22], LCD-displays [21], and others [23]. Cellulose acetate is usually prepared from cellulose with high α-cellulose contents (more than 95 %) such as purified cotton linters and wood pulps.

In present work an optimal method for extracting cellulose from OISW and converting it into cellulose acetate was developed. The properties of the obtained cellulose powder and cellulose acetate were thoroughly investigated.

Experimental

Materials

All reagents were purchased from the Aldrich Chemical Company, and used as received unless otherwise specified. Kraft pulping was performed using a high Parr Reactor model: Buchiglasuste, BMD 300. Fresh OISW was obtained from an olive factory near the city of Tulkarm in the West Bank and stored in a freezer between −5 and 0 °C.

Methods

Infrared (IR) spectra were registered using a Nicolet 6700 Fourier transform infrared (FTIR) spectrometer equipped with the Smart SplitPeaî micro-ATR accessory. Thermo Electron's OMNIC software was used for treatment of spectral data. The smart SplitPea is a horizontal attenuated total reflectance micro sampling accessory for Thermo Electrons Nicolet FT-IR spectrometers. The SplitPea is designed for analysis of very small samples of bulk solids, powders, and liquids using the ATR technique. The accessory has a diamond ATR crystal. The following parameters were used: resolution 4 cm^{-1}, spectral range 225–4000 cm^{-1}, number of scans 128.

^{1}H NMR spectra were recorded on Varian Gemini 2000, 300 MHz instrument with $(CD_3)_2SO$ as solvent and $(CH_3)_4Si$ as internal standards. All ^{1}H-NMR experiments are reported in δ units.

The size exclusion chromatography (SEC) was performed on gel-permeation chromatography/High-performance liquid chromatography (GPC/HPLC) combination; the HPLC (1260 infinity from Agilent) consisted of HPLC solvent degasser, Quaternary pump, injector, and a UV detector. The GPC detectors were an 18-angle light scattering detector the DAWN® HELEOS® II (Wyatt Technology) and the Refractive Index detector Optilab® T-REX (Wyatt Technology). The data acquisition was carried out in 0.5 s intervals with the ASTRA 6.1 software (Wyatt Technologies Corp.). The mobile phase 0.5 % LiCl/DMAc was filtered through 0.25 μm pore filters Millex LCR (Millipore) prior to use.

The separation was carried out on a set of three columns that are connected on a series, the columns are 3 × PLgel 10 μm MIXED-B, 300 × 7.5 mm (Agilent). They were placed in a thermostatted heating compartment at 25 °C and the system was operated at 25 °C with a flow rate of 1 mL/min. The mobile phase bottle was kept under a slight positive pressure of nitrogen gas. The injection volume was 100 μL and the run time was 40 min.

Calibration was done by Wyatt technology with HPLC-grade toluene filtered with 0.02 μm filter Anotop 25. Normalization was carried out on-line (with the columns) with polystyrene 30000 g/mol at 0.5016 g/mL in 0.5 % LiCl/DMAc. The refractive index of 0.5 % LiCl/DMAc was considered to be the same as that of DMAc ($n = 1.436$).

Moisture content was determined according to Tappi standard T 210 cm-03 [24]. Ash content was determined using the standard Tappi method T 211 om-02 [25]. Pulp viscosity and degree of polymerization were determined according to standard process ISO 5351-1 [26], which involve the dissolution of the pulp in an aqueous solution of copper ethylene diamine using a Cannon–Fenske viscometer. Kappa number was determined using the TAPPI standard method T236 cm-85 [27]. Electron microscopy sciences (EMS) analysis was performed using Hitachi S-3400 N variable pressure SEM system coupled with the Oxford EDS system.

Pulping of olive mill solid waste

Extraction of olive industry solid waste

Residual materials were removed using the soxhlet extraction method. OISW (200.0 g, OD weight 80 %) was added to a round bottom flask (1.0 L) of soxhlet extractor and subjected to extraction with ethyl acetate (500 mL).

The extraction was continued for 4 h. Then ethyl acetate solvent was removed under reduced pressure using a rotary evaporator to afford 10.0 g (5.6 % based on OD weight of OISW) of pale yellow residual liquid.

Kraft pulping

Kraft pulping was conducted on the extracted pulp in a high Parr Reactor of one liter capacity. In all experiments, the liquor to OISW ratio, cooking temperature, temperature rising time, holding time, and operational pressure were 4:1, 160 °C, 30 min, 90 min, and 50 psi, respectively. Active alkali charge is defined as [$NaOH + Na_2S$], and sulfidity is defined as [$Na_2S/(NaOH + Na_2S)$], where the concentrations are expressed as g/L Na_2O. Active alkali and sulfidity levels ranging from 12.5 to 15 % and from 8 to 32 % (based on the oven dried pulp), respectively, were investigated. At the end of pulping, the produced pulp (cellulose left over after the pulping process) was collected by suction filtration, washed several times with tap water, air-dried at room temperature, and stored in plastic bags for further use.

Pulp bleaching

Bleaching of pulp obtained from OISW was performed using bleaching sequence DEHP, for which the individual stages were carried out as follows:

D-stage Conducted in plastic container at 10 % consistency, for 1.0 h at 70 °C, and 1.0 % ClO_2 (based on pulp weight), with an end pH of approximately, 2.5.

E-stage Conducted in a plastic bag at 10 % consistency for 90 min at 60 °C and with 5 % NaOH (5 % based on pulp weight). After the completion of the treatment the produced pulp was filtered and washed several times with water until neutral filtrate was obtained.

H-stage Conducted in a plastic bag at 10 % consistency for 60 min at 60 °C and at a pH of 10. Hypochlorite charge of 2.5 % based on pulp weight. NaClO was obtained from a stock solution that contained 5 % of NaClO.

P-stage Conducted in a plastic bag at 10 % consistency, for 60 min, at 60 °C and a pH of 9–11 and with 2 % H_2O_2, 0.5 % $MgSO_4.7H_2O$, and 3.0 % NaOH (based on pulp weight). The mixture was filtered, washed with water until neutralization, and air-dried [28–30].

Preparation of cellulose triacetate (CTA)

The dissolution of cellulose powder was activated by the polar solvent exchange method [31]. The activation was achieved by stirring cellulose (5.0 g) in a deionized water (100 ml) at room temperature, followed by two consecutive exchanges of 1 h each with 100 ml methanol, and ended by two consecutive exchanges with 100 ml anhydrous *N*,*N* dimethylacetamide (DMAc). The first DMAc exchange lasted for 1 h and the second was prolonged overnight. After each exchange, the activation solvent was removed from the mixture by filtering under vacuum using a glass centered funnel. After the last DMAc exchange, the activated cellulose was transferred to a two necked round bottomed flask equipped with a magnet stir bar and condenser, the flask was connected to a tarp via the condenser. A solution of LiCl (19.5 g) in 300 ml DMAc was added to the flask. The mixture was stirred until a clear gel was obtained after 3.0 h. To the gel was added via a syringe triethylamine (10.0 ml), after 5 min from the addition of triethylamine, acetyl chloride (7.8 ml, 1.1 eq./hydroxyl group) was added dropwise to the reaction mixture via the addition funnel, and reaction continued for about 3 h. Then it was diluted with water, separated product was washed with plenty of tap water and air-dried to afford CTA (8.5 g, 0.03 mol) in 95.5 % yield. ^{1}H-NMR of CTA $(CD_3)_2SO$) δ (ppm): 1.92 (Me-1), 2.01 (Me-2), 2.10 (Me-6), 3.65 (H6), 3.81 (H4), 3.95 (H6b), 4.35 (H6a), 4.52 (H1), 4.75 (H2), 5.15 (H3).

Results and discussion

Pulping process

OISW was first extracted with ethylacetate to remove residual olive oil then subjected to kraft pulping, results are summarized in Table 1.

Kraft pulping was carried out at 160 °C. Pulping below this temperature produces pulp with high contents of particles that were not totally delignified, so temperature below 160 °C is insufficient for the delignification of OISW. When the temperature was raised to 160 °C, OISW was completely disintegrated into micro fibers. Various pulp properties were determined according to the standard

Table 1 Pulping conditions and pulp characteristics

Run	Pulping conditions		Pulp yield (%)	Kappa number	Viscosity (cP)
	Sufidity (%)	Active alkali			
1	12.5	8	44.5	38.2	2.42
2	12.5	16	43.3	37.1	2.31
3	12.5	24	41.0	35.6	2.28
4	15	32	38.0	32.4	2.13
5	15	8	45.1	37.6	2.39
6	15	16	42.6	36.1	2.24
7	15	24	40.3	33.2	2.11
8	15	32	36.8	29.8	1.96

Table 2 Bleaching results for samples 1 and 8 shown in Table 1

Sample	Intrinsic viscosity (cP)	Kappa number	Lignin contents	Ash contents (%)
1	1.92	1.33	0.20	0.27
8	1.77	1.30	0.20	0.23

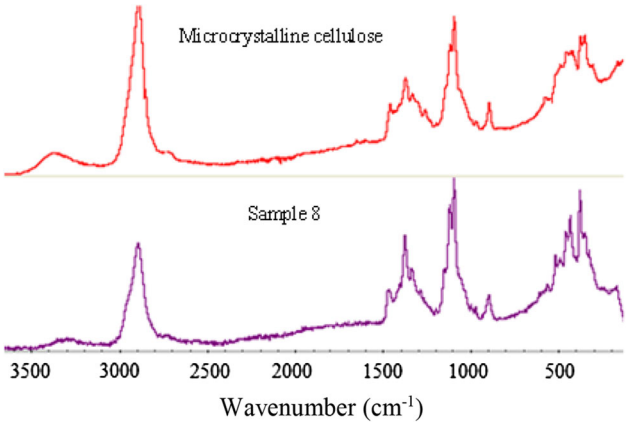

Fig. 1 IR spectra of cellulose powder sample No. 8 and microcrystalline cellulose obtained from Aldrich Chemical Company

methods mentioned earlier. The results obtained from the pulping experiments are summarized in Table 1.

Bleaching processes

Pulp samples 1 and 8 (Table 1) obtained using the kraft method were subjected to the ECF bleaching sequences DEHP in an attempt to achieve high purity cellulose that is suitable for making specialty polymers such as cellulose esters and ethers. Results are summarized in Table 2, the amount of residual lignin (kappa number), pulp viscosity (η) which is indicative of the size of the cellulosic chain, and the ash contents show that the pulp is suitable starting material for specialty polymers.

Pulp analysis

Infrared spectroscopy

The IR spectrum of sample 8 (Table 2) is shown in Fig. 1, which also includes the IR spectrum of cellulose powder obtained from Aldrich Chemical Company. As shown from the Fig. 1, the two IR spectra are almost in complete match. This could be an indication that the material extracted from OISW is actually high purity cellulose powder. The band at 3350 cm^{-1} could be attributed to hydrogen bonded hydroxyl group (OH) stretching vibration. The bands at 2920 and

Table 3 Average Mn, Mw, and polydispersity (PD) of the extracted cellulose powder samples and cellulose triacetate

	Mn ($\times 10^3$ g/mol)	Mw ($\times 10^3$ g/mol)	Polydispersity (Mw/Mn)
Pulp 1 IV 1.77	71.5	95.3	1.3
Pulp 8 IV 1.92	72.1	104.8	1.5
CTA from pulp 1 IV 1.77	40.2	74.7	1.9
CTA from pulp 8 IV 1.92	48.2	75.5	1.6

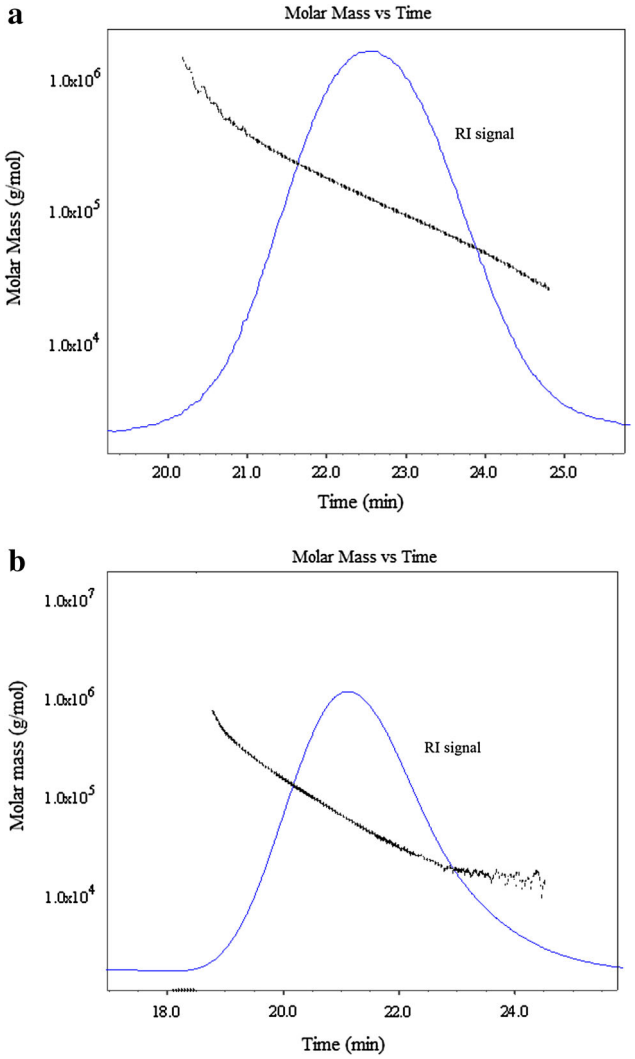

Fig. 2 a Molar mass distribution across elution time for cellulose powder sample No. 8 in 0.5 % LiCl/DMAc. b Molar mass distribution across elution time for cellulose triacetate prepared from cellulose powder sample No. 8 in 0.5 % LiCl/DMAc

2845 cm^{-1} correspond to the CH starching vibration in CH and CH_2 in anhydroglucose units of cellulose. The 1430 cm^{-1} band could be attributed to CH_2 asymmetric

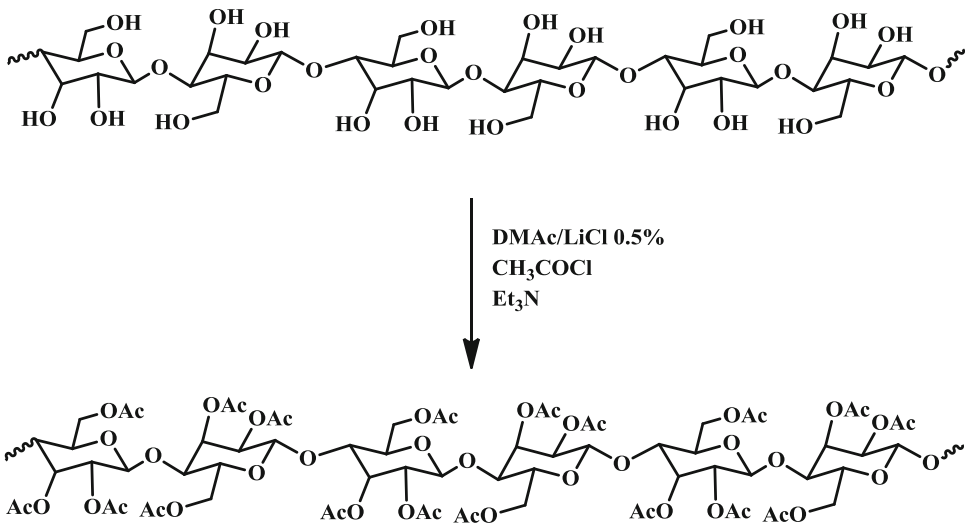

Fig. 3 A representative reaction diagram for converting cellulose powder into CTA

bending. The band at 1380 cm^{-1} corresponds to the C–O stretching of ether and alcohol groups. The band at 1160 cm^{-1} corresponds to C–O–C stretching of β-glycosidic linkage. The IR spectrum shows no peaks in the area of 1700 cm^{-1} that would be characteristics of carbonyl group in hemicelluloses. From this we could conclude the absence of hemicelluloses in the extracted cellulose powder. Also the absence of 3070 and 1600 cm^{-1} band is an indication of the absence of lignin.

Gel permeation chromatography (GPC) analysis of extracted cellulose

GPC analysis was performed on cellulose powder sample 8 and the CTAs prepared from it. Cellulose powder was dissolved in a solution of 8.0 % LiC/DMAc according to the procedure shown in the experimental section. GPC analysis results are summarized in Table 3 and in Fig. 2a. Figure 2a shows the molar mass versus the elution time (Et) in addition to the refractive index signal (RI). The molar mass distribution is represented by the black line and the RI signal is the blue curve. As shown in Fig. 2b the cellulose powder showed a linear relationship of molar mass with Et across most of the elution range. This indicates a normal elution with no column retention. The *dn/dc* value (0.077 mL g^{-1}) of cellulose solutions of 0.5 % LiCI/DMAc used in the calculation of Mn and Mw was obtained from the literature [32].

Cellulose triacetate

Extracted cellulose powder (Table 2) was converted into cellulose triacetate using a homogenous reaction method. Cellulose powder was dissolved in a solution of 0.5 % LiCl/DMAC and then reacted with acetyl chloride in the presence of triethylamine. A representative chemical reaction for converting cellulose powder into CTA is shown in Fig. 3. The homogenous method used in this work is industrially infeasible, it was chosen to show the potentiality of the OISW as a feed stock for the value added material cellulose acetate. However, other method like the acetic acid heterogeneous method is industrially more convenient and lower in cost. It should be no difference between CTA prepared by the heterogeneous method or the acetic acid method except that, the molar mass of CTA prepared by the acetic acid method could be lower, since sulfuric acid used as a catalyst in the homogenous method depolymerizes cellulose polymer chain.

In the homogenous method cellulose powder was first activated by the solvent exchange method shown in the experimental part, and then dissolved in a solution of 6.5 % LiCl/DMAc. Dissolved cellulose powder then reacted with

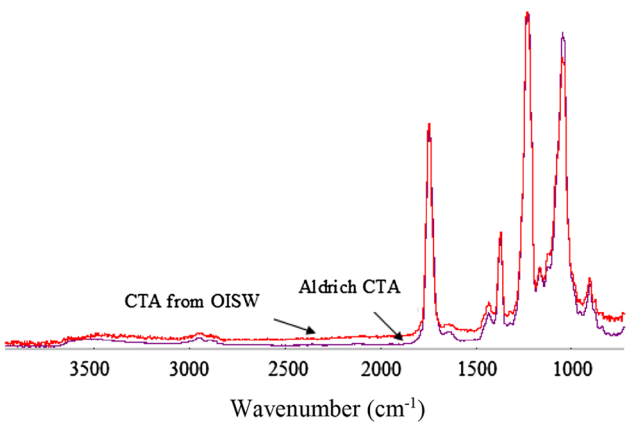

Fig. 4 FTIR of cellulose triacetate prepared from cellulose powder extracted from OISW and cellulose triacetate obtained from Aldrich

excess acetyl chloride and triethyl amine. The acetylation was conducted with quantitative yield (95.5 %). Prepared samples of CTA were analyzed by various analytical and spectroscopic techniques, such as: FTIR, GPC, ^{1}H NMR. The IR spectrum of prepared CTA is shown in Fig. 4, which also includes the IR spectrum of cellulose acetate with acetate contents of 40 % (degree of substitution is 2.68) obtained from Aldrich Chemical Company. As shown in Fig. 4, the two IR spectra are in almost complete match. This could be an indication that the material extracted from OISW is actually high purity cellulose acetate with a degree of substitution close to 2.68. The comparison between the FT-IR spectra of cellulose powder (Fig. 1) and cellulose acetate (Fig. 4) demonstrates the functionalization of the anhydroglucose units, since two new absorption bands appear at 1730 cm^{-1} and at 1270 cm^{-1} due to the C = O stretching and to the –C–O– stretching of the acetate functional group introduced the forming of cellulose acetate.

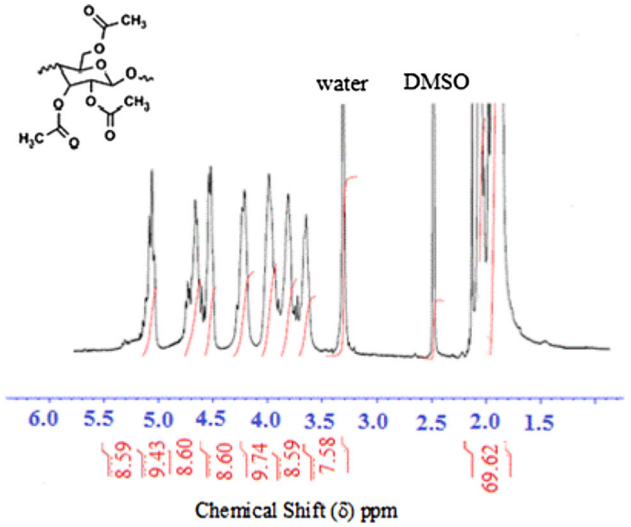

Fig. 5 ^{1}H NMR of cellulose triacetate prepared from cellulose powder sample No. 8

The ^{1}H NMR spectrum of the prepared CTA is shown in Fig. 5, the spectrum shows the five methane protons, the two methylene protons of the anhydroglucose repeat unit (3.7–5.2), and the three methyl protons of acetyl groups (1.8–2.1 ppm). Chemical shifts and integration of the seven protons and the methyl protons are consistent with those reported in the literature [33].

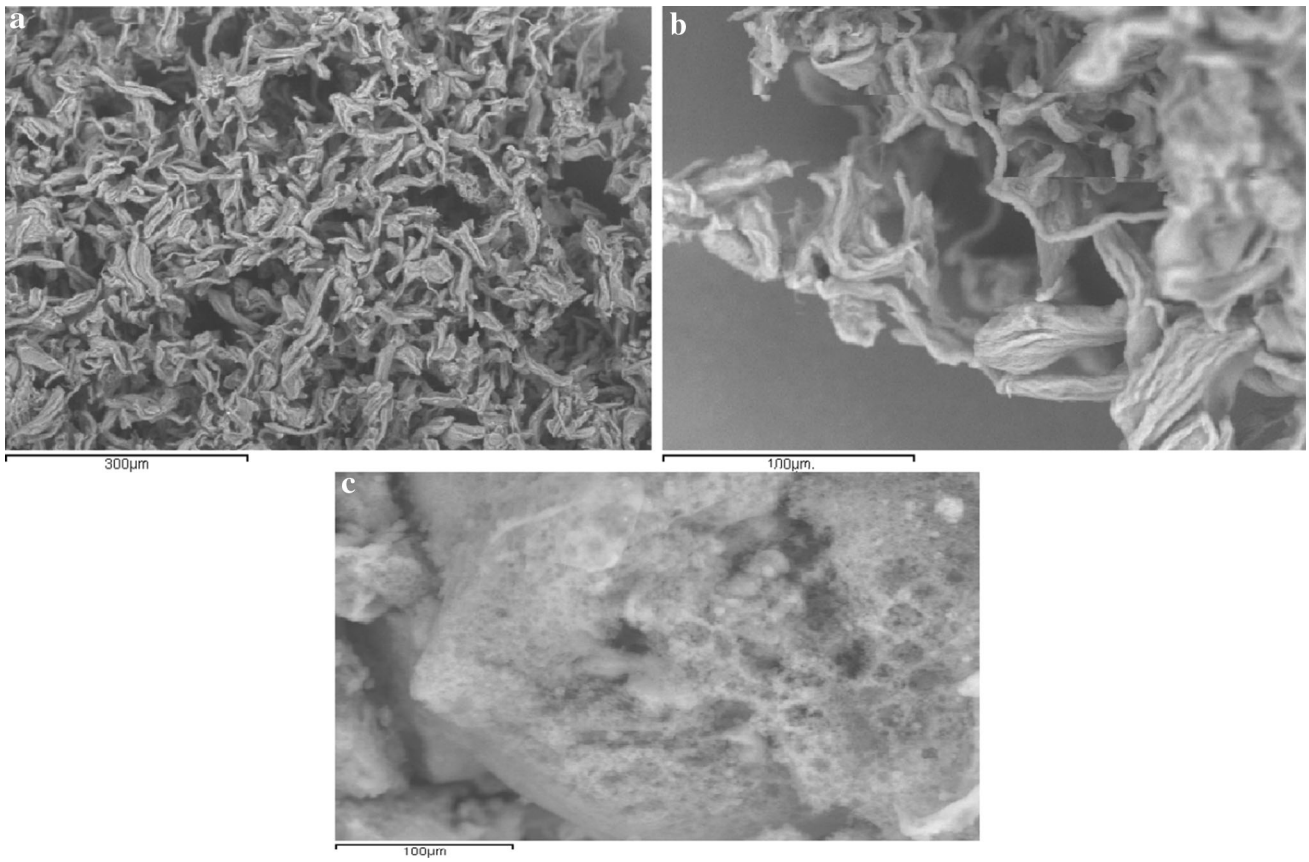

Fig. 6 SEM images of cellulose powder sample No. 8 at two magnifications; a 50×, b 200×, and c SEM image of CTA at a magnification of 1000×

GPC analysis of CTA

Cellulose triacetate prepared form cellulose extracted from OISW was also analyzed by GPC. The results are summarized in Table 3 and the obtained chromatogram is shown in Fig. 2b. Like in the case of cellulose powder (Fig. 2a). CTA showed a linear relationship of molar mass with Et across the elution range. The *dn/dc* value (0.048 mL g^{-1}) for CTA in solutions of 0.5 % LiCl/DMAc used in the calculation of Mn and Mw was obtained from the literature [34]. As shown in Table 3, even the reaction was performed in cellulose none hydrolyzing solvent a lower values of Mn and Mw are shown than were anticipated. This could be attributed to the partial hydrolysis of CTA by HCl produced as side product during the course of the reaction.

Scanning electron microscopy (SEM) of cellulose powder and CTA

Cellulose powder extracted from OISW was also investigated by scanning electron microscope (SEM). Figure 6a, b show the SEM images of cellulose powder at two different magnifications 50× and 200×. These images clearly show that MCC particles have a regular flat shape with semi porous surface. From Fig. 4b, the diameter of cellulose powder was found to be ca. 6.5 μm. Figure 4c shows an image of CTA at a magnification of 1000×. As shown in the image, CTA has a spongy structure.

Degree of substitution

Degrees of substitution (DS) of CTA was determined as reported in the literature by titration with an aqueous solution of sodium hydroxide to be about 2.76 [35] and by ^{1}H NMR spectroscopy to be 2.65 [33]. In the ^{1}H NMR method, the average integration of each of the seven protons (8.7) of the anhydroglucose repeat unit was calculated by dividing the total protons integration (61.7) over the number of protons (7). The total integration of the three methyl protons (9 protons) of the acetyl groups in the range of 1.8–2.1 ppm (69.62) was divided by the average proton integration 8.7, and the results was divided by 3 (3 methyl groups) to produce number of methyl groups per anhydroglucose repeat unit.

Conclusions

A quantitative method for obtaining cellulose powder from solid waste material of the olive industry was developed. In this method, cellulose powder was extracted from OISW by conventional kraft pulping, and then subjected to various bleaching sequences. The best result was obtained with ECF bleaching sequence DEHP. Cellulose powder was obtained in about 34 % yield. The materials extracted form OISW turned out to be a suitable precursor of cellulose derivatives such as cellulose esters. Extracted cellulose was converted in a quantitative yield into cellulose acetate under mild conditions by dissolving it in a non hydrolyzing solvent and by carrying the acetylation reaction at room temperature. The prepared acetates were then characterized in terms of chemical and physical structure, showing the degree of substitution and molecular weight comparable to those of commercial reference materials. The cellulose acetate made from cellulose powder extracted from OISW could be suitable for cellulose films and packaging materials.

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