Biomass Conversion and Biorefinery (2024) 14:14627–14639
https://doi.org/10.1007/s13399-023-03739-3

ORIGINAL ARTICLE

Multiproduct biorefinery from defatted olive mill waste: preparation of hemicellulose-based biodegradable films and instant controlled pressure drop (DIC)-assisted isolation of value-added products

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Received: 31 August 2022 / Revised: 27 December 2022 / Accepted: 31 December 2022 / Published online: 25 February 2023

Abstract

The olive oil extraction industry generates huge amounts of olive mill waste (OMW) which is an excellent source of several biocompounds. The aim of this study is to investigate the viability of a multiproduct biorefinery approach to valorize OMW as a source of hemicelluloses for the production of biodegradable films and extraction of other valuable compounds by taking advantage of the instant controlled pressure drop (DIC) technique. Glycerol, sorbitol, and xylitol at a concentration of 30% (w/w) were found as suitable plasticizers for biodegradable film preparation. Films with glycerol showed the lowest solubility in water (73.25 ± 0.83%) and the lowest biodegradability in soil, while showing the highest water vapor permeability (1.82 ± 0.1 g mm m^{-2} h^{-1} kPa^{-1}), and lowest solubility in different media at pH of 3–12. Xylitol-plasticized films exhibited the highest tensile strain (10.17 ± 0.85 MPa) which is 43% higher than that of unplasticized film. Overall, the glycerol-plasticized films showed a potential for food packaging applications where low solubility and high water vapor permeability are required. Xylitol-plasticized films could be advantageous where higher solubility and mechanical strength are expected. DIC pretreatment performed at 5 bar steam pressure for 10 min resulted in a destructured OMW with lower crystallinity providing higher extraction yields of value-added products. An increase of 37.5% in total phenolics content and 22.1% in hemicellulose extraction yield were obtained after DIC pretreatment, respectively. In addition, app. 3-fold antioxidant activity and 2.2-fold reducing sugar concentration were reached, as compared to unpretreated OMW.

Keywords Olive mill waste · Biorefinery · Hemicellulose · Biodegradable film · Controlled instant pressure drop · Pretreatment

1 Introduction

In recent years, food waste and agricultural biomass management has become a global concern. The biorefinery approach, which covers integrated biomass conversion processes, could play a crucial role in sustainable and zero-waste global development [1]. The primary purpose of the biorefinery is to minimize process waste, obtain high value-added products and improve the economy. For this purpose, in biorefinery facilities, biomass is converted into multiple chemicals and energy products by integrated methods (mechanical/thermal, biological, inorganic solvent, organic solvent, and unconventional physical–chemical); thereby increasing the commercial value of the substrate and reflecting positively on the profitability while reducing the amount of waste [2, 3]. Agro-bioenergy co-products and agricultural residues are potential candidates for the production of second-generation biofuels and high-added value co-products through an integrated biorefinery approach [4]. For example, the fruit and vegetable processing industry generates by-products such as peels, seeds, and shells which contain bioactive components such as antioxidants, pigments and flavor compounds, proteins, essential oils, enzymes, and dietary fibers at high concentrations [5]. Based on that, the valorization of biological resources (e.g., agricultural by-products and wastes,

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lignocellulosic biomass, food waste) leads to the development of many value-added products (biocomposites, bioplastics, biomaterials, and biofuels) providing several advantages such as reduced CO_2 emissions, lower toxicity, and biodegradability [6].

The olive oil production process involves crushing of olives and separation of oil from the remaining components (pomace). Olive pomace has been reported as a good source for hydroxytyrosol and tyrosol derivatives, flavonoids (rutin, apigenin, luteolin, quercetin), tocopherols and tocotrienols, lignans (pinoresinol), phenolic acids (cinnamic, p-coumaric, caffeic, ferulic, and vanillic acids), monounsaturated and polyunsaturated fatty acids as well as dietary fiber, minerals, and oligosaccharides [7]. The pomace is further processed to extract the remaining oil by solid–liquid extraction with hexane. The resulting biomass (defatted olive pomace or defatted olive mill waste, OMW) representing 18–25% of olive weight [8] is mainly used as solid biofuel [9] or spread on land as fertilizer [10]. However, dangerous particles and gases emitted during energy production by combustion make this technology non-desirable [8]. Due to the high organic content and phyto-toxicity potential of OMW, its net effect on crops and soil microflora is questionable if used in high amounts in soil [10]. OMW is a lignocellulosic feedstock containing cell wall polysaccharides (cellulose, hemicellulose, and pectin) up to 49% by weight [11]. Therefore, processing the OMW in a sustainable and environmentally friendly way to obtain high value-added products is of great interest in the context of a biorefinery, based on olive-derived biomass [12].

Biodegradation is defined as the mineralization of organic material by microorganisms, which results in the final products CO_2 and water under aerobic conditions [13]. Bioplastics are obtained from biopolymers and they are biodegradable under most general conditions. However, bioplastics should be distinguished from synthetic bio-based plastics (e.g., PLA) which are not always biodegradable [13]. Biodegradable films are attracting attention based on their potential to help to improve the efficiency of food packaging, and thus offering a supplementary effect over reducing the use of petroleum-derived polymers [14]. Based on their compatibility with the requirements of green chemistry, hemicellulose and its composites have been extensively used for biodegradable food packaging applications, as a renewable and environmentally friendly alternative to petroleum-based plastics [15]. However, applications of hemicelluloses in food packaging are hindered by inherent problems, such as brittleness, poor film-forming properties, and low mechanical strength [16]. Physical and chemical modification methods are commonly employed to improve the performance of hemicellulose films because the unmodified hemicellulose films often show poor mechanical properties due to their branched and amorphous structures [17].

In order to overcome these difficulties, plasticizers are added to the hemicellulose matrix as a physical modification approach to break the hydrogen bonds between the polymer chains and increase the chain mobility [16]. Different plasticizers have been investigated for hemicellulose-based films, such as glycerol [16], sorbitol [18], and xylitol [16]. Not only the plasticizers, but also the type of the lignocellulosic biomass has an important effect on the formation of intact hemicellulose-based films [18]. Therefore, using different plasticizers (glycerol, sorbitol, xylitol) together with OMW hemicelluloses in order to obtain continuous and self-supporting hemicellulose-based films with improved physical properties was investigated in this study.

Instant controlled pressure drop technology (Détente Instantanée Contrôlée; DIC) is a type of hydrothermal treatment (French patent no. 93/09726) which was firstly used to dry and texture various biological products [19], and later explored as a method for extraction [20, 21]. DIC is a thermo-mechanical technique which subjects the sample to high-pressure dry steam for a short period, followed by a sudden pressure drop close to a vacuum [19]. During this process, a sudden pressure drop in the vacuum causes the vaporization of water and swelling of the matrix by the breakdown of the cell wall. A new expanded structure is obtained with an increased specific surface area and enhanced mass transfer properties. Therefore, solvent diffusivity within a solid is improved. Since the accessibility of the biomass is increased, the extraction yield also increases [22]. This process appears to be an advantageous technique for the pretreatment of OMW, in terms of the extraction of valuable components.

The main objective of this work was to valorize OMW as a biomass feedstock for the production of value-added bioproducts. For this aim, two approaches were followed. Firstly, OMW hemicellulose was isolated by the alkaline extraction method (without using any harsh physical/thermal pretreatment) from untreated OMW and used in the preparation of plasticized biodegradable films. The films were then physically characterized. In the second approach followed, the effect of DIC pretreatment on the extraction yield of other valuable components of OMW was studied. In addition to its hemicellulose content, untreated and DIC-treated OMW was investigated in terms of the extraction yield of phenolics, antioxidants, and production of reducing sugars. Besides, changes in crystallinity and morphological structure of OMW caused by DIC pretreatment were detected by FTIR and SEM.

2 Materials and methods

2.1 Materials

Defatted OMW samples (10 kg) were kindly provided by an oil processing plant (Uşaklı Pirina) located in

İncirliova-Aydın (Turkey). OMW was ground and passed through a 0.425 mm sieve. OMW was analyzed in terms of moisture (method 44-15A, AOAC 1998), ash (method 08–01, AOAC 1998), fat (method 30–10, AOAC 1998), protein (method 46–30, AOAC 1998), and crude fiber content (method 920.86, AOAC 1998) [23]. The results of the compositional analysis of OMW are presented as the mean (standard deviation, ± SD) of triplicate analysis. All chemicals used were of analytical grade and were purchased from Sigma-Aldrich (USA), Merck (Germany), and VWR (USA) companies. They are used as received without any further purification.

2.2 Extraction of OMW hemicelluloses

Extraction of hemicelluloses was performed by following the protocol described by Zilliox and Debeire [24] with slight modifications. Ground and sieved (1.2–1.4 mm) OMW of 10 g was swollen in 250 ml of water at room temperature for 30 min. The suspension was filtered and the solid phase was mixed with 80 ml of 19.3% (w/v) KOH solution for 25.3 h at room temperature in a shaking incubator (IKA KS 4000, Germany), as previously optimized for OMW by our research group [25]. Then, the sample was filtered and the cellulose fraction was separated. The supernatant was centrifuged at 10,000 rpm for 10 min using a centrifuge (Eppendorf 5804, Germany) to remove insoluble particles. Following the centrifugation, the precipitation solution (1:10 volumetric ratio of acetic acid to ethanol) with a volume of 2.5 times the volume of the supernatant was added to the alkaline solution. The precipitate (hemicellulose fraction) was collected by centrifugation at 10,000 rpm for 10 min, dried in an incubator (Nüve EN 400, Turkey) at 45 °C until constant weight and used for biodegradable film production.

2.3 Preparation of the films

Films were prepared by solvent casting method. The hemicellulose fraction (0.5 g) was dissolved in 20 ml of distilled water by stirring for 1 h at 90 °C, and at room temperature for another 24 h. Plasticizers; glycerol (Gly), sorbitol (Sor), and xylitol (Xyl) were added to the film-forming solution at specified concentrations (5–30 g plasticizer/100 g hemicellulose). The solutions were stirred for 6 h for complete mixing and poured into plastic Petri dishes (9 cm internal diameter). The samples were incubated (dried) in a climatic test chamber (Nüve TK120, Turkey) at 50% relative humidity (RH) and 23 °C temperature. The films named as HC (neat hemicellulose film), HC-Gly (glycerol-plasticized HC), HC-Sor (sorbitol-plasticized HC), and HC-Xly (xylitol-plasticized HC) were peeled-off from the Petri dishes and used for further studies.

2.4 Characterization of the films

2.4.1 Film thickness

Film thickness was determined as the average of five measurements (between the edge and the center) for each film sample using a digital micrometer (0.001 mm accuracy) (Mitutoyo, Japan). The average film thickness data was used for the assessment of the tensile strength and water vapor permeability (WVP) of the films.

2.4.2 Film color

Color measurement of the films was performed using a HunterLab device (HunterLab Color Flex CFLX-45, USA) by using a HunterLab color scale (L^*, a^*, b^*). The color of the films was measured at five different points after calibrating with a standard white plate and the results; L^* (lightness), a^* (greenness/redness), and b^* (blueness/yellowness) are expressed as mean ± SD. The total color difference (ΔE) was calculated according to Eq. 1.

$$\Delta E^* = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2} \quad (1)$$

where ΔL^*, Δa^*, and Δb^* are the difference between each color parameter of the film samples and of the white calibration plate.

2.4.3 Tensile strength (TS)

TS of the films were evaluated with film specimen strips (2 cm × 6 cm) using the tensile testing equipment (TA-XT Plus, Stable Micro Systems, UK) equipped with a 5-kg load cell and mini tensile grips A/MTG 14,534 (Stable Micro Systems, UK). The films were conditioned at 23 °C and 50% RH prior to testing. The samples were mounted between grips with a film width of 2 cm. Five replicates were tested for each sample and the results of TS (MPa) were expressed as mean ± SD.

2.4.4 Film water solubility (FWS)

The film specimens (conditioned at 23 °C and 50% RH for 24 h) were cut into a square piece of 3 cm × 3 cm and brought to constant weight (m_1) at 70 °C in an incubator (Nüve EN 400, Turkey). Film samples were submerged in 10 mL of distilled water for 1 h in a shaking incubator (IKA KS 4000, Germany) at 150 rpm. The samples were removed from the water and dried at 70 °C to constant weight (m_2). FWS (%) was calculated according to Eq. 2.

$$\mathrm{FWS}(\%) = \frac{[(m_1 - m_2)]}{m_1} \times 100 \quad (2)$$

2.4.5 Water vapor permeability (WVP)

The WVP of the films was determined according to the ASTM E96/E96M-16 method [26] with slight modification. Film samples without any physical defects were sealed onto cylindrical glass containers (permeability cells) (100 ml volume, 5.4 cm diameter) containing 30 ml of distilled water using epoxy glue (Pattex). After recording their initial mass, the permeability cells were placed in a climatic test chamber (Nüve TK120, Turkey) at 23 °C and 50% RH. The cells were weighed regularly at 24 h intervals for 7 days and the variation of mass versus time was plotted. The water vapor transmission rate (WVTR) was calculated from the slope of the fitted straight line (g/h) divided by the test area (test cell mouth area) (m^2). WVP was calculated from Eq. 3 [27].

$$\mathrm{WVP} = \frac{[\mathrm{WVTR}(\frac{g}{hm^2})] \times [\updownarrow(mm)]}{[\Delta P(\mathrm{kPa})]} \quad (3)$$

where WVP: water vapor permeability (g mm m^{-2} h^{-1} kPa^{-1}), WVTR: water vapor transmission rate (g m^{-2} h^{-1}), ℓ: film thickness (mm), ΔP: the difference between the partial pressure (P_0) of the water vapor on the surface of the film outside the test cell (50% RH) and the partial vapor pressure (P_i) of the water inside the test cell (100% RH) at test temperature (23 °C).

2.4.6 Stability of the films in water, acid, and alkali

In order to evaluate the stability of the films in water, acidic and alkaline media, film samples of 3 cm in diameter were cut and immersed in 10 ml of distilled water, hydrochloric acid (pH 3), and sodium hydroxide (pH 12), respectively. The visual changes in the film samples after 24 h were observed.

2.4.7 Film biodegradability in soil

The biodegradability of films in soil was investigated by following the method described by Jaramillo et al. [28]. The commercial garden soil was placed in a plastic tray (10 cm × 25 cm × 5 cm) to a height of 4 cm. Sample films 3 cm × 3 cm were buried in the soil with an aluminum net to a depth of app. 1 cm and the tray was incubated at room temperature. Biodegradation was started at natural soil moisture content and the soil was water sprayed on a daily basis to sustain the soil moisture. Residues of films were removed with tweezers and the images of the films were recorded regularly every 2 days for a period of 10 days of degradation in soil.

2.5 Instant controlled pressure drop (DIC) pretreatment

OMW was pretreated using lab-scale DIC equipment composed of four main parts, namely steam generator, stainless steel processing vessel (10 L), vacuum chamber (app. 70 L), and a large diameter valve capable of opening rapidly (< 1 s, for 100% valve opening). The technical details and schematic diagram of the DIC equipment used were presented in our previous study [29]. The vacuum pressure in the vacuum chamber was kept constant at 100 mbar in the DIC system and the opening ratio of the valve was chosen as 100% throughout all the experiments. OMW (10 g, ground and passed through a 0.425 mm sieve) was placed in the processing chamber. The OMW sample was exposed to saturated steam at 5 bar pressure for 10 min. Then, the large diameter valve was suddenly (0.2 s) opened to reduce the steam pressure (5 bar) to the vacuum pressure (100 mbar). The process was terminated when the pressure of the processing chamber balanced with the atmospheric pressure. The DIC-treated OMW sample was dried at room temperature and used for further analysis.

2.5.1 Scanning electron microscopy (SEM)

Morphological changes in OMW caused by DIC treatment were visualized using the Hitachi SU 5000 FE-SEM (Japan) device. The samples were coated with gold–palladium using a vacuum coater (LEICA EM ACE200, Germany) before analysis. Sample images were observed at 500–1500 × magnification with a voltage of 3–15 kV.

2.5.2 Fourier transform infrared spectroscopy (FTIR)

The FTIR spectrum of the untreated and DIC-treated OMW was recorded from 4000 to 400 cm^{-1} with a resolution of 4 cm^{-1} on a Vertex 70 ATR-FTIR spectrometer (Bruker, UK) at room temperature.

2.6 Component analysis after DIC pretreatment

2.6.1 Total phenolics

Ground and sieved (0.425 mm) OMW (5 g) was extracted with acidified methanol (HCl:methanol:water, 10:80:10, v/v) at room temperature for 2 h on a magnetic stirrer. The extract was centrifuged at 10,000 rpm for 10 min using a centrifuge (Eppendorf 5804 Model, Germany). The supernatant was used for total phenolics content (TPC) determination. TPC of the untreated and DIC-treated OMW was evaluated

according to the Folin-Ciocalteu method using gallic acid as the standard [30]. TPC was expressed as mg of gallic acid equivalents (GAE/g OMW).

2.6.2 Antioxidant activity

The extract was obtained using acidified methanol as described in Section 2.6.1. Antioxidant activity was measured using 2,2-diphenyl-l-picrylhydrazyl (DPPH) scavenging ability analysis according to Beta et al. [31]. The extract (100 µl) was reacted with 3.9 ml DPPH solution (2.4 mg of DPPH in 100 ml of methanol). The mixture was incubated at room temperature for 2 h and the absorbance (A) was determined spectrophotometrically (Shimadzu UV-1800, Japan) at 515 nm. Methanol was used as the blank. The results are expressed as IC_{50} (the concentration with 50% scavenging activity).

2.6.3 Hemicellulose recovery

In order to determine the effect of DIC treatment on the yield of hemicellulose extraction from OMW, the alkaline extraction method reported by Zilliox and Debeire [24] was followed with slight modification. The OMW sample (5 g) was stirred in 125 ml of distilled water for 15 min at room temperature and the solid phase was separated by filtration. The solid phase was mixed with 42.5 ml of KOH solution (24%, w/v) and incubated at room temperature for 24 h under continuous stirring. After stirring, the suspension was filtered and the solid particles were removed by centrifugation at 5000 rpm for 5 min using a centrifuge (Eppendorf 5804 Model, Germany). The hemicellulose fraction was precipitated by adding 125 ml of ethanol-acetic acid (10:1, v/v). The precipitate was obtained by centrifugation at 10,000 rpm for 5 min and was brought to constant weight at room conditions. The hemicellulose extraction yield (%, w/w) was calculated from Eq. 4 as the ratio of the dry mass of extracted hemicellulose (m_2) to the initial mass of OMW (m_1).

$$\text{Hemicelluloseyield}(\%) = \frac{m_2}{m_1} \times 100 \quad (4)$$

2.6.4 Reducing sugars

Enzymatic hydrolysis of untreated and DIC-pretreated OMW was performed using xylanase from *Scytalidium thermophilum* (ATCC no. 1645). The enzyme was produced as described previously [32] and the enzyme activity assay was performed according to the procedure reported by Bailey et al. [33]. The reaction mixture (10 ml) contained 1% (w/v) OMW sample and 30 IU mL^{-1} enzyme in 50 mM sodium phosphate buffer at pH 7. The reaction was carried out at 45 °C with gentle stirring and samples were taken from the reaction mixture after 24 h for the reducing sugar analysis. The reducing sugars liberated by enzymatic hydrolysis of biomass samples were determined with the dinitrosalicyclic acid (DNS) method [34] by using xylose as the standard.

3 Results and discussion

3.1 Compositional analysis of OMW

The moisture content of OMW was found as 6.3 ± 0.04% and the chemical composition of OMW on a dry weight basis is determined using moisture content data. Ash, fat, protein, and crude fiber contents of OMW were found to be 2.4 ± 0.1%, 3.2 ± 0.2%, 7.6 ± 0.4%, and 46.2 ± 1.6%, respectively. The results are in agreement with those reported by Dermeche et al. [35] as 1.7–4.0% for ash and 2.87–7.26% for protein. The fat content of OMW appeared to be lower as a result of the treatment with hexane to remove the remaining oil from OMW. The crude fiber content of the OMW was 46.2%, comprised of mainly cellulose and acid-insoluble lignin. The remaining part of OMW (34%) is potentially composed of acid soluble lignin, hemicellulose, and soluble extractives like monomeric and oligomeric sugars (glucose, xylose, arabinose, mannose) and acetyl group compounds. According to a recent study by Gómez-Cruz et al., olive pomace was mainly composed of app. 42% aqueous-ethanolic extracts, 22% lignin, 20% of structural carbohydrates (cellulose and hemicelluloses), and 10% of sugars such as glucose and xylose [36], as compatible with the results of the present study.

3.2 Characteristics of the films

3.2.1 Effect of plasticizers

Plasticization helps to increase the workability of the biopolymers and to handle the brittleness of the films by breaking hydrogen bonds between polymer chains [16, 37]. Low-molecular-weight polyols Gly, Sor, and Xyl are added as plasticizers to the hemicellulose matrix in this study. The appearances of films with different concentrations (5–30%, w/w) of plasticizers are presented in Fig. 1. Gly, Sor, and Xyl were totally miscible with hemicellulose matrix and they hindered brittleness of the films; hence, self-standing and continuous films were obtained at 30% (w/w) concentration (Fig. 1). Films plasticized with Gly, Sor, and Xyl at 30% (w/w) concentration were used for further studies.

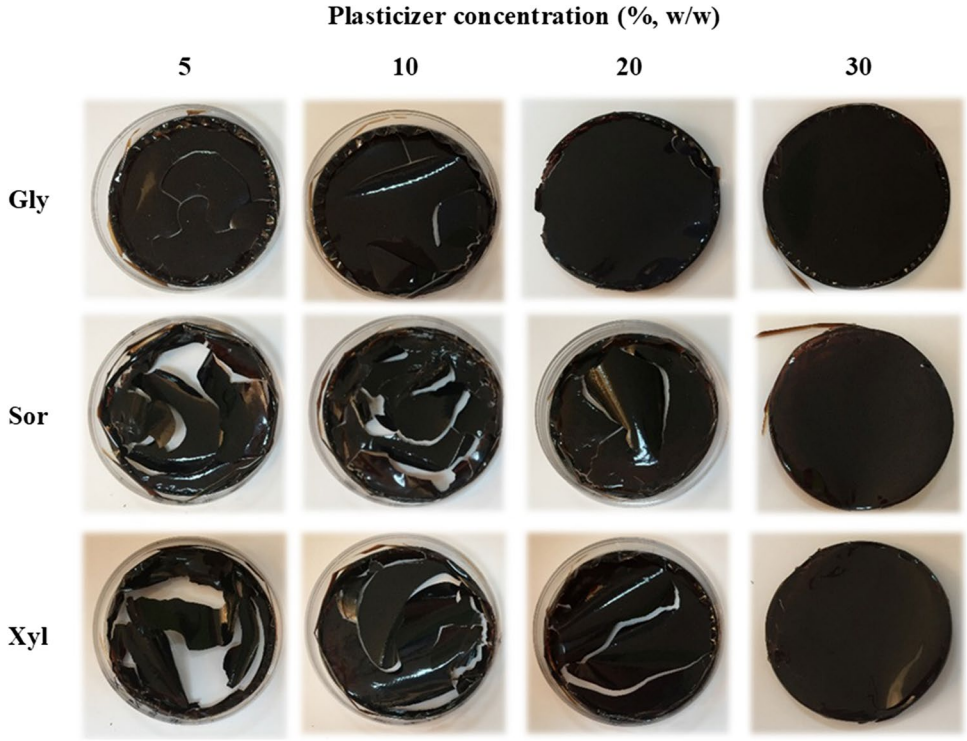

Fig. 1 Effect of plasticizers on biofilm structures. Gly: Glycerol, Sor: Sorbitol, Xy:l Xylitol

3.2.2 Thickness and color

The effects of the incorporation of different plasticizers on the thickness and color of the films are presented in Table 1. HC had lower thickness compared to the plasticized films (HC-Gly, HC-Sor, HC-Xyl). The incorporation of all the tested plasticizers caused a decrease in L^* values; hence, the plasticized films were darker in color. The highest color difference (ΔE^*) values were observed with HC-Gly and HC-Xyl. In contrast, HC-Sor exhibited a very similar ΔE^* value compared to HC. All film samples showed homogenous appearances and were black in color (Fig. 1). Although transparent and colorless films are preferred in the food industry to ensure the visibility of the product, the black color of the films provides a great advantage for the protection of packaged food products from photooxidative agents [38]. From this point of view, OMW hemicellulose films have a potential to be superior to existing biodegradable films, especially in the packaging of foods with a high risk of oxidation catalyzed by light.

3.2.3 Film water solubility (FWS), water vapor permeability (WVP), and tensile strength (TS)

FWS is an important property for biodegradable films, which differs from water permeability [16]. As can be seen in Table 2, HC-Gly showed lower FWS (73.25 ± 0.83%) as compared with HC (81.60 ± 1.36%). In contrast, FWS of films increased after the incorporation of Sor and Xyl. As given in Table 2, the WVP of the films increased significantly (62.5%) with incorporating of Gly (HC-Gly). The addition of Sor (HC-Sor) and Xyl (HC-Xyl) also increased the WVP, but to a lesser extent (%16–17). All of the hemicellulose-based films exhibited higher WVP (in the range of 1.12–1.82 g mm m^{-2} h^{-1} kPa^{-1})

Table 1 Thickness and color of the films

Sample	Thickness (μm)	L^*	a^*	b^*	ΔE^*
HC	58 ± 12	16.59 ± 0.99	−0.40 ± 0.15	−0.85 ± 0.08	77.35
HC-Gly	87 ± 15	10.02 ± 1.71	−0.55 ± 0.08	−0.86 ± 0.07	92.92
HC-Sor	75 ± 19	15.15 ± 0.29	−0.61 ± 0.05	−0.37 ± 0.16	78.79
HC-Xyl	70 ± 23	3.55 ± 1.09	−0.15 ± 0.10	−0.62 ± 0.09	90.38

Hemicellulose film (HC) plasticized with glycerol (HC-Gly), sorbitol (HC-Sor), and xylitol (HC-Xyl). L^*, a^*, and b^* are Hunter Lab color parameters. White calibration plate (L^* = 93.92, a^* = −1.02, b^* = 0.26) was used as film background. Values reported for thickness are the mean ± standard deviation of testing two replicates at five different points and for color are the mean ± standard deviation of five replicates

Table 2 Water solubility (FWS), water vapor permeability (WVP), and tensile strength (TS) of the films

Sample	FWS (%)	WVP (g mm m^{-2} h^{-1} kPa^{-1})	TS (MPa)
HS	81.60 ± 1.36	1.12 ± 0.07	7.11 ± 0.08
HS-Gly	73.25 ± 0.83	1.82 ± 0.10	7.17 ± 0.23
HS-Sor	89.88 ± 0.96	1.31 ± 0.01	4.48 ± 0.69
HS-Xyl	85.36 ± 0.23	1.30 ± 0.06	10.17 ± 0.85

Hemicellulose film (HC) plasticized with glycerol (HC-Gly), sorbitol (HC-Sor), and xylitol (HC-Xyl). Values reported are the mean ± standard deviation of four replicates for TS, and triplicate analysis for FWS and WVP

in comparison to the commercial LDPE packaging film (0.03 g mm m^{-2} h^{-1} kPa^{-1}). Xu et al. [16] reported slightly higher FWS and WVP results for the films containing plasticizers (Gly, Sor, Xyl) as compared with the unplasticized films. The reason may be attributed to the relatively lower interactions between the polymer chains caused by the incorporation of plasticizers [16], hence, increasing the level of the plasticizers increases the WVP of the films [39]. The findings of this study are consistent with the results from Zhang and Whistler [39]. They reported higher WVP for Gly-plasticized arabinoxylan films as compared to Sor-plasticized films. This result is associated with the bulky and poorly hygroscopic structure of Sor, which makes it less able than Gly to affect hydrogen bonding between polysaccharide chains [39]. Xyl-plasticized films (HC-Xyl) have the highest TS (10.17 ± 0.85 MPa) as expected from the lower WVP values for HC-Xyl compared to HC-Gly and HC-Sor.

3.2.4 Stability in water, acid, and alkali

The stability of biodegradable films subjected to different pH conditions is of great importance due to their potential interaction with a wide range of pH, especially in the food industry [28]. The neat and plasticized films were immersed in water, acidic (pH 3), and alkaline (pH 12) media for 24 h to assess their stability (Fig. 2). HC and HC-Gly swelled app. 1.3 times with respect to their initial dimension under water, acidic, and alkaline conditions. Specifically, HC-Gly showed the lowest solubility in all media. HC-Sor and HC-Xyl completely dissolved in all media after 24 h. The stability of HC-Gly at all tested pH conditions is important considering the possible use of these films for a wide range of products in the food market [28]. HC-Sor and HC-Xyl dissolve at a higher rate compared to HC. This behavior is of great importance when fast dissolution is required, e.g., packaging films of instant food products.

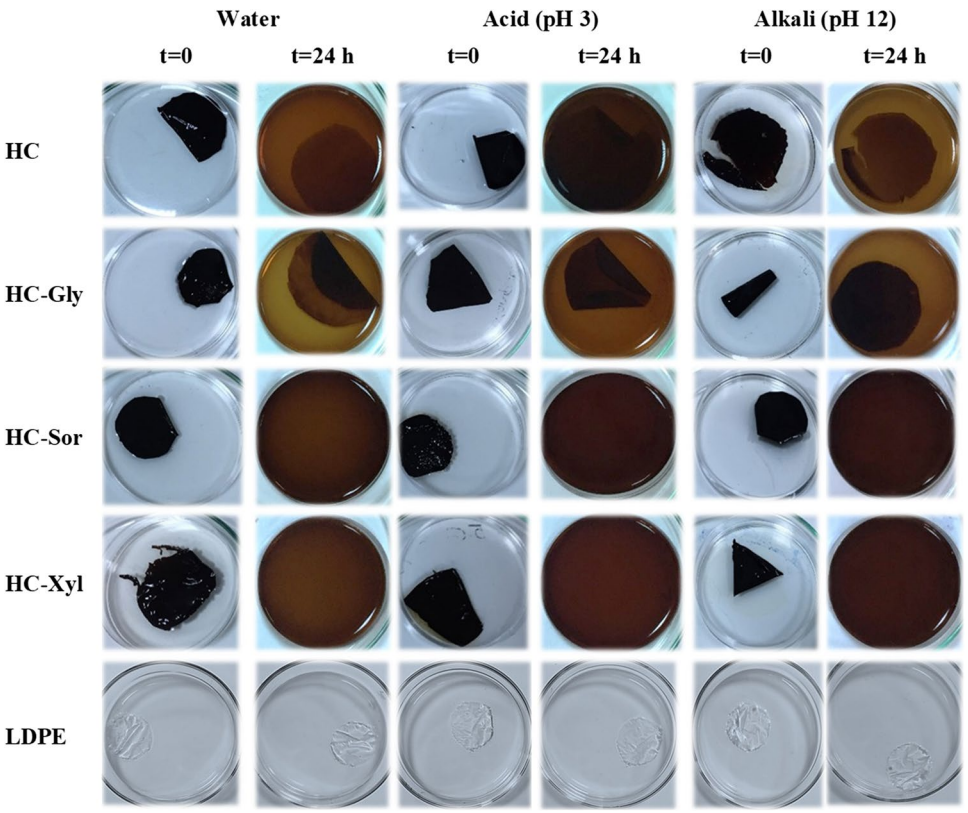

Fig. 2 Stability of films immersed in water, acidic, and alkaline media after 24 h. All the film samples had a 3 cm diameter at the beginning of the test. Hydrochloric acid (pH 3) and sodium hydroxide (pH 12) were used to facilitate acidic and basic conditions, respectively

3.2.5 Biodegradability

A comparative and qualitative analysis of the biodegradability of hemicellulose-based films was performed. A low-density polyethylene (LDPE) film was tested as a control. The quantitative analysis was not possible due to the residual soil on the buried film samples. The visible degradation of HC began on the 2nd day of the burial of the samples whereas the degradation of all the plasticized films (HC-Gly, HC-Sor, HC-Xyl) started on the 4th day (Fig. 3). In the previous study, the decomposition of bulgur bran HC films started on the 6th day of the experiment [27]. Among the plasticized hemicellulose-based films, HC-Gly was found to have the lowest decomposition rate (Fig. 3). The uptake of moisture is often a crucial factor in the rate of degradation [40]. Therefore, lower FWS (Table 2) and higher stability in different aqueous media (Fig. 2) of HC-Gly have been considered to be related to its low biodegradability. In addition, high stability in the acidic and alkaline environments of HC-Gly also contributes to its slower decomposition.

3.3 Effect of DIC on multiproduct biorefinery of OMW

3.3.1 Crystallinity analysis by FTIR

In order to investigate the changes in crystallinity of OMW samples after DIC pretreatment, FTIR spectroscopy analysis before and after DIC pretreatment was performed. The FTIR spectra of OMW samples are illustrated in Fig. 4. The profile of the FTIR spectra was different for unpretreated and DIC-pretreated OMW samples showing structural changes of the lignocellulosic matrix. Peaks between 800 and 1200 cm^{-1} are generally difficult to interpret because they are referred to a compound-specific fingerprint region [41]. However, the

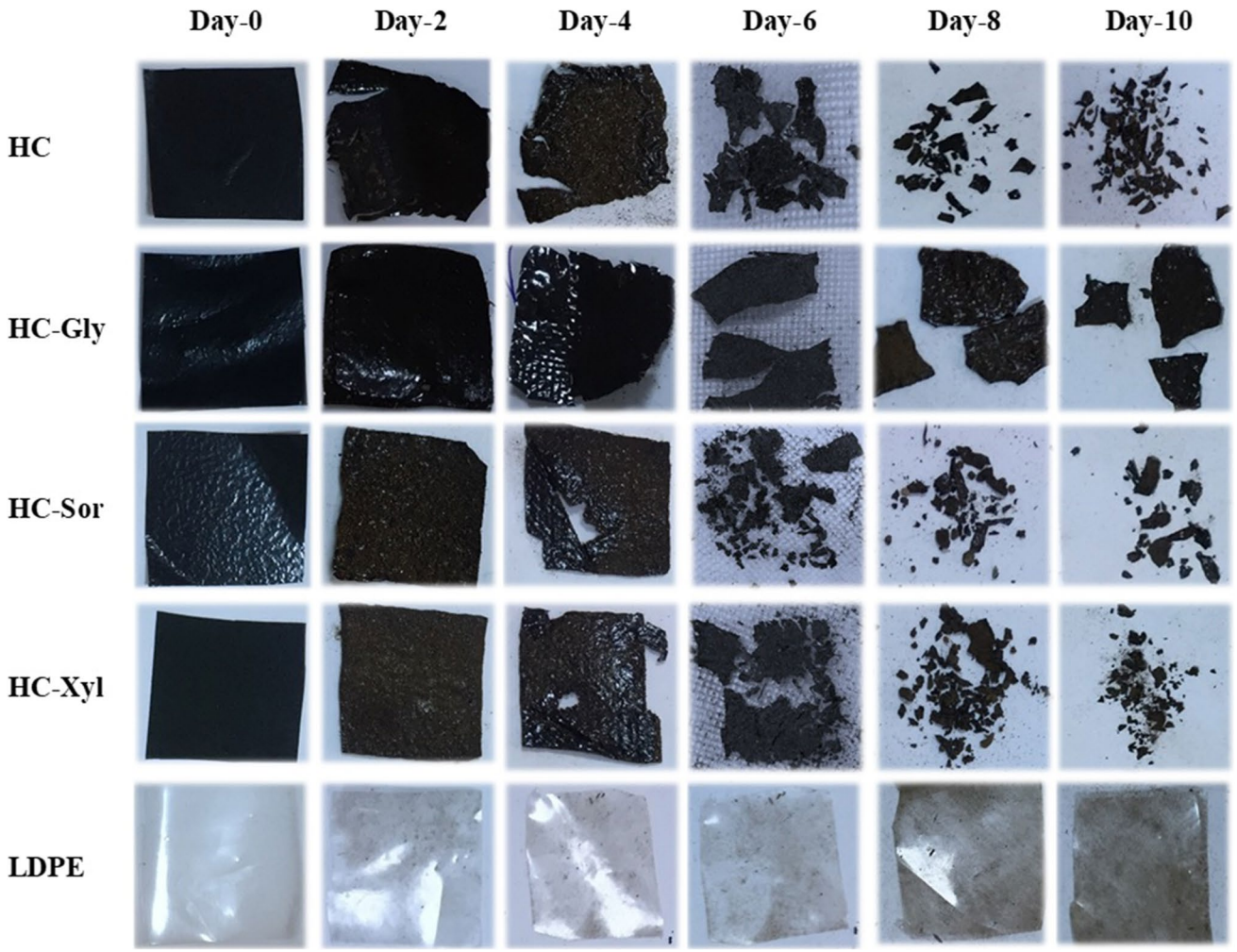

Fig. 3 Biodegradability of the biofilms in soil. The films 3 cm × 3 cm were buried in garden soil in a plastic tray (10 cm × 25 cm × 5 cm)

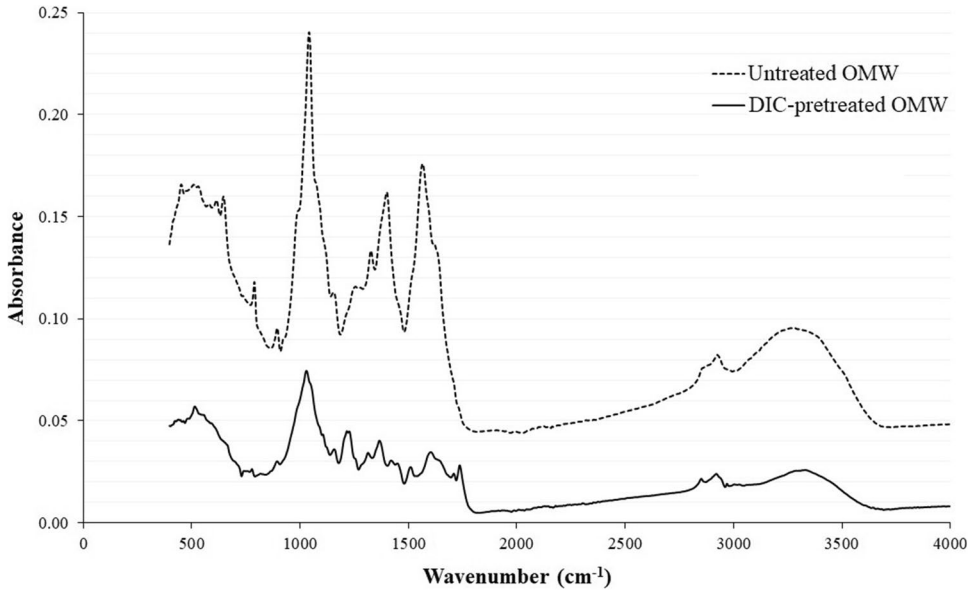

Fig. 4 FTIR spectra of OMW

peak at 1045 cm^{-1} for both untreated and DIC-treated OMW spectra is assigned to the C–O and C–C stretching vibration and the glycosidic linkage (C–O–C) contributions showing the presence of hemicelluloses [42].

FTIR is a rapid and noninvasive method enabling measurement of the crystallinity of the material, expressed as crystallinity indexes: lateral order index (LOI) (the ratio between 1427 cm^{-1}/895 cm^{-1} bands) and total crystallinity index (TCI) (the ratio between 1373 cm^{-1}/2900 cm^{-1} bands) [43]. LOI and TCI showed lower values for DIC-pretreated OMW samples (1.212 and 0.953) compared to the untreated OMW (1.854 and 1.786), respectively (Table 3). While cellulose, hemicellulose, and lignin in the lignocellulosic matrix are strongly bonded through covalent and non-covalent bonds, a recalcitrant structure is formed [44]. Specifically, intra- and intermolecular hydrogen bonds between cellulose chains lead to high crystallinity which causes resistance to the enzymatic digestibility of cellulose and accessibility of other valuable components. The results of LOI and TCI suggest a less ordered cellulose structure in OMW after DIC pretreatment, hence, a decrease in crystallinity. Lower crystallinity is expected to facilitate an enhanced OMW fractionation and higher extraction yields of value-added compounds.

3.3.2 Total phenolics content (TPC) and antioxidant activity

TPC of OMW (15.2 mg/g untreated sample) increased after DIC pretreatment (20.9 mg/g total treated sample) (Table 3), which might be attributed to disruption of hemicellulose and lignin and decreased crystallinity after DIC pretreatment, as observed during the recovery of phenolic compounds from OMW by steam explosion process [45]. In contrast to the results of the present study, Serrano et al. [45] found that the total phenolic content of the solid phase fraction of OMW after steam treatment was 14 g gallic acid/kg total volatile solid, which was lower than that of untreated OMW (24 g gallic acid/kg total volatile solid). In the present study, the DIC process provided a higher phenolic recovery in solid phase extraction of OMW with respect to the untreated sample, which corresponds to a 37.5% increase in TPC. Similarly, Seçmeler et al. [46] obtained the highest phenolic recovery (4512.4 mg/100 g) for pre-treated olive pomace with steam treatment at 200 °C for 5 min. However, the increase was only 11% in their study. The positive impact

Table 3 Effect of DIC on crystallinity (LOI and TCI), total phenolics content (TPC), antioxidant activity, hemicellulose recovery, and reducing sugar concentration

Sample	LOI	TCI	TPC (mg GAE/g OMW)	Antioxidant activity (IC_{50}, mg OMW/ml)	Hemicellulose yield (%, w/w)	Reducing sugar concentration after 24 h hydrolysis (mg/ml)
Untreated OMW	1.212	1.854	15.2 ± 1.0	11.0	19.0 ± 1.2	1.22
DIC-pretreated OMW	0.953	1.786	20.9 ± 1.5	3.6	23.2 ± 1.7	2.74

of DIC pretreatment on phenolics was demonstrated by the studies of Mounir et al. [21] for quercetin in apple powder and Sánchez-Valdepenas et al. [47] for gallic acid, quercetin, ellagic acid, and resveratrol in grape stalk powder. They observed that DIC treatment had a greater effect than the solvent used in the extraction process.

DIC pretreatment improves the extraction characteristics of the samples due to structural expansion under an instant thermo-mechanical process [20]. As shown by the SEM images (Fig. 5), DIC pretreated OMW displayed smaller and heavily distorted surfaces in comparison with the untreated OMW. The new structure is supposed to have a higher specific surface area and higher mass transfer diffusivity. Similar results were obtained by Eikani et al. [48], showing that DIC treatment was effective in improving the diffusivity and permeability of safflower and castor seeds by increasing the surface of an area of the matrix through instant pressure drop, as observed in the present study.

DIC-pretreated OMW showed higher antioxidant activity, where the DIC-pretreated sample had an IC_{50} value of 3.6 mg OMW/ml. This value surpassed the control with an IC_{50} value of 11.0 mg OMW/ml, resulting in a 3-fold increase (Table 3). A similar result for the beneficial effects of DIC pretreatment is reported by Ranjbar et al. [49], who observed a maximum increment of 12% in the antioxidant capacity of the DIC-pretreated pomegranate peel sample, analyzed by the DPPH method. A most recent study by Alonzo-Macías et al. [50] showed that coupling DIC as a blanching-steaming pretreatment provided a better preservation of the antioxidant content and the antioxidant activity of dried red beetroots.

3.3.3 Hemicelllulose yield

The hemicellulose yield obtained from DIC-pretreated OMW (23.2%, w/w) was higher than the yield corresponding to the untreated OMW (19.0%, w/w) (Table 3). The chemical composition of olive pomace varies according to the variety of the olive and the extraction process. According to Miranda et al. [51], structural components of the extracted olive pomace included 31.2% lignin, 13.8% glucan, and 22.7% hemicellulose. Recently, Domenech et al. [52] reported the chemical composition of the extracted dry olive pomace which presented a rather low content of cellulose (11%) and hemicellulose (12%). Steam diffuses into the plant cell wall, causing hemicellulose hydrolysis and lignin transformations through high temperature in the steam explosion process [53]. DIC pretreatment of OMW facilitated a 22.1% increase in hemicellulose extraction yield. In contrast to DIC treatment, Rincón et al. [54] showed that steam explosion pretreatment of OMW diminished the hemicellulose content of OMW from 11.3 to 5.8%, due to hydrolyzation of hemicelluloses to simple sugars by auto-hydrolysis [54].

Hemicelluloses are relatively sensitive to operation conditions such as temperature and retention time [55]. Degradation temperatures of different hemicelluloses ranged from 243 (xylan) to 332 °C (arabinoxylan, xyloglucan, and β-glucan) [56]. During the DIC treatment, the temperature of the saturated steam was 158 °C, where the vapor pressure was 5 bar, in the present study. This temperature is far below 243 °C and it is possible to obtain hemicellulose with minimal degradation using DIC pretreatment. Manzanares et al. [57] observed that the xylan content of olive pomace was reduced from 11.7 to 1.2% (dry base) as the temperature of extraction rose (from 170 to 210 °C), respectively. DIC pretreatment remarkably improved the extraction characteristics of the samples due to structural expansion under an instant thermo-mechanical process. The surface area increased by DIC pretreatment caused easier diffusion of the solvent through the structure, causing increased hemicellulose yield [57].

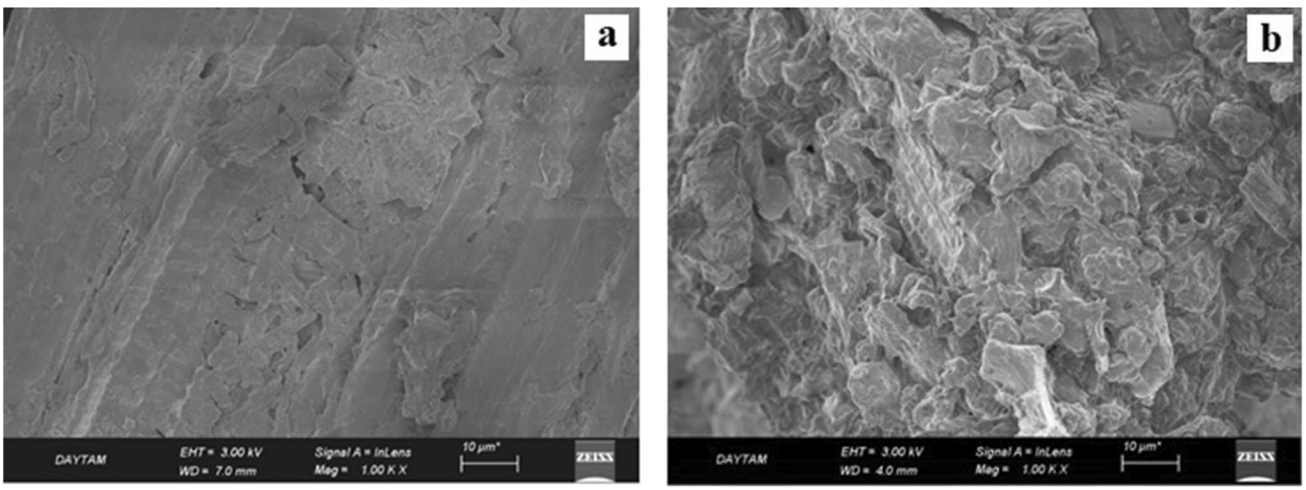

Fig. 5 Images of OMW obtained via scanning electron microscopy (SEM) **a** Untreated OMW, **b** DIC-pretreated OMW

3.3.4 Reducing sugar content

The effectiveness of xylose production from biomass is principally evaluated by the degree of conversion of hemicellulose to xylose monomers. Therefore, the effect of the DIC pretreatment on the enzymatic hydrolysis of OMW for the purpose of reducing sugar production was also evaluated. Upon enzymatic conversion of OMW, DIC-pretreated OMW had a 2.2-fold reducing sugar concentration than the untreated counterpart (Table 3). The results of the present study share a number of similarities with the findings of Messaudi et al. [58]. They observed a significant increase in saccharification yields after the DIC pretreatment of lignocellulosic biomass (eucalyptus chips and Aleppo pine cones), due to the opening of lignocellulosic structures and the modification of the physical properties of the biomass. DIC pretreatment modified the structure of the OMW (Fig. 5), as previously discussed. The SEM image of untreated OMW presented a rough and more intact structure while the image of DIC-pretreated OMW displayed an open and destructed matrix, thus, increasing the surface area of the biomass. Hereby, SEM images support the higher efficiency of the enzymatic hydrolysis and production of reducing sugars at increasing amounts from OMW after DIC pretreatment [58].

4 Conclusions

This study presents OMW as a potential feedstock for the production of hemicellulose-based biodegradable films and value-added products through the multiproduct biorefinery approach. OMW is obtained in amounts of millions of tons annually as the waste of the olive oil extraction industry and could be used as a feedstock for hemicellulose-based biodegradable film production. Polyols (glycerol, sorbitol, and xylitol) have been found suitable plasticizers for the production of self-standing, flexible, and biodegradable OMW hemicellulose films. Combination of OMW hemicellulose with other polymers can result in biofilms with enhanced barrier properties. In combination with their black color, OMW hemicellulose films could be potential future packaging materials, especially for food products having the risk of light-catalyzed oxidation. In addition, considering the necessity to develop valorization processes for the waste biomass, OMW has been shown to be a potential feedstock for the production of value-added products through the multiproduct biorefinery approach. As a thermo-mechanical pretreatment strategy, DIC helped to obtain higher extraction yields for phenolics, antioxidants, hemicelluloses, and reducing sugars by reducing the recalcitrance of OMW. DIC technique was especially helpful to extract heat labile bioactive compounds from OMW by increasing diffusivity, so it is applicable to many types of the industrial wastes/by-products to increase their usage and bioavailability. The authors suggest that future work should be focused on the complete fractionation of OMW by using DIC-assisted pretreatment processes to valorize cellulose and lignin fractions, in addition to hemicellulose. Besides, implementation potential in the industry of DIC-treated OMW samples for hemicellulose-based bioplastic applications should be verified after complete fractionation and purification processes.

Abbreviations *AOAC*: Association of Official Analytical Chemists; *DIC*: Instant controlled pressure drop (Détente Instantanée Contrôlée); *DNS*: Dinitrosalicyclic acid; *DPPH*: 2,2-Diphenyl-l-picrylhydrazyl; *FTIR*: Fourier transform infrared spectroscopy; *FWS*: Film water solubility; *Gly*: Glycerol; *HC*: Unplasticized hemicellulose film; *HC-Gly*: Glycerol-plasticized hemicellulose film; *HC-Sor*: Sorbitol-plasticized hemicellulose film; *HC-Xyl*: Xylitol-plasticized hemicellulose film; IC_{50}: The concentration with 50% scavenging activity; *LDPE*: Low-density polyethylene; *LOI*: Lateral order index; *OMW*: Olive mill waste; *PLA*: Polylactic acid; *RH*: Relative humidity; *SD*: Standard deviation; *SEM*: Scanning electron microscopy; *Sor*: Sorbitol; *TCI*: Total crystallinity index; *TS*: Tensile strength; *TPC*: Total phenolic content; *WVP*: Water vapor permeability; *WVTR*: Water vapor transmission rate; *Xyl*: Xylitol

Acknowledgements The authors would like to thank Karamanoğlu Mehmetbey University Scientific and Technological Research Application and Research Center (BİLTEM) for SEM analysis. The authors also thank Karamanoğlu Mehmetbey University Department of Bioengineering for FTIR analysis.

Author contribution Conceptualization: Didem Sutay and Sibel Yağcı; Methodology: Didem Sutay and Sibel Yağcı; Formal analysis and investigation: Eren Yurtdaş and Merve Toptaş; Writing—original draft preparation: Didem Sutay and Sibel Yağcı; Writing—review and editing: Didem Sutay, Sibel Yağcı, Eren Yurtdaş, and Merve Toptaş; Funding acquisition: Didem Sutay.

Funding This work is partially funded by Karamanoğlu Mehmetbey University (KMU-BAP Project no. 22-M-17).

Data availability The datasets generated during the current study are available from the corresponding author on reasonable request.

Declarations

Ethical approval Not applicable.

Competing interests The authors declare no competing interests.

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