PLA coating improves the performance of renewable adsorbent pads based on cellulosic aerogels from aquatic waste biomass

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Abstract

Lightweight, hydrophobic, adsorbent pads based on aerogels from different cellulosic and nanocellulosic fractions extracted from *Posidonia oceanica* waste biomass were developed by a simple freeze-drying and PLA dipping method. The pure (nano)cellulosic aerogels presented highly porous structures, capable of adsorbing large amounts of oil (up to ~34 g oil/g aerogel); however, they lost their integrity when soaked in water. The incorporation of PLA hydrophobized the aerogels and improved significantly their mechanical performance (up to 10-fold increase in the compression stress). The most porous aerogel structures, obtained with the lowest (nano)cellulosic concentrations and with the less purified fractions, incorporated greater amounts of PLA upon dipping, which was mostly distributed filling in the pores. All the PLA-coated (nano)cellulosic aerogels presented a hydrophobic behavior, with contact angles of 95-130° and selectively adsorbing greater amounts of oil (5.9-9.2 g oil/g aerogel) than water (2.8-6.7 g H₂O/g aerogel). These materials present a great potential as adsorbent pads for oil spill cleaning and food packaging applications.

Keywords: porous materials; *Posidonia*; seaweed; biopolymers; oil sorption; microstructure.

Abbreviations

PLA: Poly(lactic acid)

F2A: Cellulosic fraction obtained by omitting both Soxhlet and KOH treatments

F2: Cellulosic fraction obtained by omitting the KOH treatment

F3A: Cellulosic fraction obtained by omitting the Soxhlet treatment

F3: Pure cellulose fraction

NANO F2A: Nanocrystals obtained from F2A

NANO F2: Nanocrystals obtained from F2

NANO F3A: Nanocrystals obtained from F3A

NANO F3: Nanocrystals obtained from F3

1. Introduction

The large increase in population over the last century, together with the globalization of the markets and the consumerist society have generated a significant increase on the demand of goods and services. As a result, large amounts of residues are generated worldwide, being plastic materials one of the most abundant residues. Synthetic plastics are widely used nowadays due to their excellent mechanical performance, cost-efficiency and high chemical stability. Although the latter attribute can benefit the use of synthetic plastics in certain applications, such as food packaging (to protect the products from the external environment and extend their shelf life), it also gives rise to severe environmental issues. These materials require extremely long times to disintegrate after their disposal into landfills. Moreover, they can reach marine ecosystems, where they are transformed into the so-called micro-plastics, which are not only a great hazard to aquatic organisms [1], but can also be incorporated into the food chain, posing a threat to human health [2, 3]. In this context, circular economy policies, aiming to reduce waste through the whole production chain by the utilization of alternative natural bio-based raw materials and the application of re-valorization strategies, are currently being boosted by European governments. Not only alternative renewable resources are being studied to replace less environmentally friendly materials, but also greener processes, reducing the use of chemicals and energy, are being explored to minimize the environmental impact of the manufacturing chain.

In the particular case of the food packaging sector, biopolymers, i.e. bio-based and biodegradable polymers, are being extensively explored for the replacement of synthetic plastics in several types of packaging structures such as trays, lids and sorbent pads [4, 5]. Each type of packaging structure needs to meet certain specific requirements and, thus, the

properties of biopolymers have to be adapted accordingly. For instance, sorbent pads are commonly used in packages to minimize the amount of excess liquids released by fresh products upon storage, although they can also be utilized as templates for the incorporation and sustained release of bioactive compounds towards the food products [6, 7]. Aerogels are extremely light and porous materials with high surface area and low density, which are useful for environmental, construction, pharmaceutical, bio-medical, food and cosmetic applications due to their high absorption and adsorption capacities [8-10]. Although aerogels have been traditionally made from inorganic materials such as silica or alumina [11, 12], their application as pads in the food packaging area requires the search of sustainable materials with properties that resemble those from the commercially used synthetic polymeric pads. In this sense, aerogels made from biopolymers such as cellulose, pectin or chitin have been recently proposed as promising materials [13]. In particular, many recent works reporting on the production of cellulose-based aerogels can be found in the literature [14-16]. Despite their great potential, the application of these materials within food packaging is still a largely unexplored area, which is mostly due to the complexity of their manufacturing processes, often involving the use of chemical agents and/or organic solvents unsuitable for food applications, and their poor performance under high relative humidity conditions [6, 17]. Cellulose-based aerogels are typically produced by complex methodologies involving an initial disruption of the crystalline structure to dissolve cellulose (through the use of ionic liquids or mercerization treatments) [16, 18], gelation, cellulose regeneration, solvent exchange and a final drying step by means of supercritical CO₂ or freeze-drying [19, 20]. Due to the highly hydrophilic nature of cellulose, the obtained aerogels are susceptible to disintegrate upon moisture contact, thus requiring the application of hydrophobization treatments. These treatments normally consist of chemical modification of cellulose, cross-

linking and/or coating with hydrophobic agents such as silanes [14, 21, 22], which are not acceptable for food-related applications and confront the sustainability and circular economy principles.

In this work, the valorization of *Posidonia oceanica* waste biomass for the production of bio-based cellulosic and nanocellulosic aerogels is proposed. Previous work has demonstrated that less purified (nano)cellulosic fractions may present superior performance than pure cellulose, while increasing the sustainability of the obtained materials [23]. Based on this, the properties of aerogels produced from different (nano)cellulosic fractions by freeze-drying of their aqueous suspensions have been evaluated. Furthermore, a simple PLA (poly(lactic acid)) dipping method has been tested for the hydrophobization and improvement of the mechanical performance of selected aerogels. The developed materials are therefore fully bio-based, adsorbent systems suitable for food packaging applications and produced by means of a cost-effective and sustainable method.

2. Materials and methods

2.1. Raw materials

Biomass waste material consisting of *Posidonia oceanica* leaves was directly collected in the sea shore of Calpe (Alicante, Spain) in January 2018. The material was washed vigorously with water in order to remove sand and stored under refrigeration (4° C) until its use.

2.2. Preparation of cellulosic fractions and nanocrystals from *Posidonia oceanica* biomass

A purification procedure described in previous works [24, 25] and consisting of a Soxhlet extraction (4 g of dry material were extracted with 800 mL of 2:1 toluene:ethanol for 24 h), followed by bleaching (the material obtained from the first step was treated for 5 h at 70 °C with 700 mL of 1.4% w/v NaClO₂) and an alkaline treatment (the material was treated with 400 mL 5% w/v KOH for 24 h at room temperature, followed by 2 h at 90 °C), was applied to sequentially remove cell wall components and obtain holocellulose (F2) and pure cellulose (F3). Less purified fractions were also obtained by omitting the Soxhlet step (F2A and F3A). These fractions were then subjected to an optimized hydrolysis treatment with sulphuric acid, as described in [23], to produce nanocellulosic materials (labelled as NANO F2, NANO F2A, NANO F3 and NANO F3A). Briefly, the fractions were immersed in a H₂SO₄ solution (30% v/v), with a ratio of 1.5 g (dry fraction) / 100 mL of H₂SO₄, and were heated to 50 °C during 2 h under stirring conditions. The obtained fractions and nanocrystals were stored in the fridge as partially hydrated gel-like materials, until further use.

2.3. Production of cellulosic aerogels

Aerogels were produced by dispersing the required amount of cellulosic or nanocellulosic materials in 15 mL of distilled water by ultra-turrax homogenization to obtain concentrations of 0.5, 1, 1.5 and 2 wt.-%. These suspensions were transferred to plastic Petri dishes (5 cm diameter), frozen at –80 °C for 4 h and then freeze-dried using a Genesis 35-EL freeze-dryer (Virtis). The obtained cellulosic and nanocellulosic aerogels were labeled according to the fraction used as starting material (F2, F2A, F3, F3A, NANO F2, NANO F2A, NANO F3 and NANO F3A).

Additionally, selected aerogels (F3, NANO F3, NANO F2A and NANO F2) were used to produce hybrid cellulosic-PLA aerogels using a proprietary technology [26]. Briefly, PLA

was dissolved in chloroform at a fixed concentration of 5% (w/v) by stirring at 50°C during 30 minutes. The (nano)cellulosic aerogels were dipped in the PLA solution for 1 minute and the samples were then dried at room temperature in a fume hood until the chloroform was completely evaporated (at least 24 h). The obtained aerogels were stored in equilibrated relative humidity cabinets at 0% RH and 25°C for at least three days prior to their characterization. The amount of PLA sorbed by the aerogels was calculated as follows:

$$\% PLA = \frac{W_f - W_0}{W_0} \times 100 \quad (1)$$

where W_0 refers to the (nano)cellulosic aerogel initial weight and W_f corresponds to the final sample weight (aerogel + PLA). At least four samples were prepared for each (nano)cellulosic aerogel type.

2.4. Scanning electron microscopy (SEM)

SEM was conducted on a Hitachi microscope (Hitachi S-4800) at an accelerating voltage of 10 kV and a working distance of 8-16 mm. Small samples (~5 mm² area) of the pure (nano)cellulosic and PLA-coated (nano)cellulosic aerogels were cut to observe their surface. The samples were then sputtered with a gold–palladium mixture under vacuum during 3 minutes before their morphology was examined.

2.5. Density of aerogels

Aerogel densities were determined from the weight and volume of each individual aerogel. The weight was determined by an analytical balance (Precisa Gravimetrics AG SERIES320XB, Dietikon, Switzerland) and the dimensions were measured by a digital calliper at three different positions.

2.6. Water and oil sorption

Squared aerogel specimens with a total surface area of 1 cm² were cut, weighed and immersed in sealed containers containing 15 mL of distilled water or sunflower oil. The samples were periodically taken out of the liquid and weighed after removing the liquid excess. Measurements were taken until the samples were equilibrated and the total weight gain was calculated. After equilibration, the samples were removed from the liquid, placed on top of aluminum foil (in the case of water) and filter paper (in the case of oil) and left drying at ambient conditions. The weight was registered periodically, until it was constant (~1 week). The water and oil retention capacity was calculated from the difference between the weight after drying and the initial weight of the samples, before soaking them in the liquids. All the measurements were carried out at least in triplicate.

The experimental curves obtained for the water and oil sorption processes were fitted using pseudo-first order and pseudo-second order models.

The pseudo-first order model is described by the following expression:

$$q(t) = q_e [1 - e^{-k_1 t}] \quad (2)$$

where $q(t)$ is the amount of adsorbed solute, q_e its value at equilibrium and k_1 is the pseudo-first order kinetic rate constant.

On the other hand, the pseudo-second order model is described by the following expression:

$$q(t) = q_e \frac{k_2^* t}{1 + k_2^* t} \quad (3)$$

where $k_2^* = k_2 \cdot q_e$ and k_2 is the pseudo-second order kinetic rate constant.

2.7. Immersion of PLA-coated (nano)cellulosic aerogels in water/oil media

To investigate the selectivity of the PLA-coated (nano)cellulosic aerogels to adsorb water and oil, a mixture of 50/50 water/sunflower oil (v/v) was prepared. Distilled water was stained with methylene blue and sunflower oil was stained with Congo red to differentiate the two media. The PLA-coated (nano)cellulosic aerogels were firstly immersed in the water phase and subsequently in the interphase between water and oil.

2.8. Contact angle measurements

Contact angle measurements were carried out at 23 ± 2 °C and ambient relative humidity (ca. 60%RH) in a Video-Based Contact Angle Meter model OCA 20 (DataPhysics Instruments GmbH, Filderstadt, Germany). Contact angle values were obtained by analyzing the shape of a distilled water drop after it had been placed over the film for 15 s. Image analyses were carried out by SCA20 software. Results were obtained from an average of at least 5 measurements.

2.9. Confocal laser scanning microscopy (CLSM)

Sunflower oil was stained by adding 0.1% (v/v) of Nile Red in ethanol (1:10 Nile Red:Oil) and vortexing vigorously until a homogeneous solution was achieved. Aerogels were then immersed in the stained oil for at least 10 minutes in order to maximize oil sorption. Immersed aerogels were then visualized using a Leica TCS SP5 confocal laser scanning microscope (Leica Microsystems CMS GmbH, Wetzlar, Germany) with 5x and 10x dry objectives (numerical apertures of 0.12, 0.30 and 0.70, respectively) and the pinhole set at 1 Airy Unit. Nile red was excited at 488 nm using an Argon laser, and the emission filter was set at 560-600 nm. A second filter set at 488 nm was also used to observe the light reflected

by the cellulosic materials. Leica LAS AV software (v 2.7.3.9723) was used to acquire digital images of 1024 x 1024 pixels in size at day 1 and 50 after immersion. Samples were placed in darkness conditions between imaging to avoid fluorescence loss.

2.10. Compression tests

Uniaxial compression tests were carried out at 20 °C on a texture analyser (Stable Micro Systems model TA-XTplus, Surrey, UK). The sample size for the compression test ranged between 8-10 mm (diameter) × 8-10 mm (thickness) with a cylindrical shape. A cylindrical aluminium probe with a diameter of 25 mm was used to compress the specimen at a compression rate of 0.1 mm s⁻¹ using a 5 kg load. Samples were analyzed at least in duplicate.

2.11. Statistics

Analysis of variance (ANOVA) followed by a Tukey-b test were used when comparing more than two data sets. All data have been represented as the average ± standard deviation. Significant differences ($p \leq 0.05$) are denoted by showing the data provided in tables and figures with different letters.

3. Results and discussion

3.1. Characterization of pure (nano)cellulosic aerogels

Initially, pure (nano)cellulosic aerogels were produced by using aqueous dispersions (0.5 wt.-%) of the cellulosic and nanocellulosic fractions extracted from *P. oceanica*. All the produced aerogels presented a sponge-like appearance (cf. Figure 1A and Figure 1B). As

observed, the degree of purification tremendously affected the integrity and structure of the aerogels, especially in the ones produced from the cellulosic fractions. While F2 and F2A (containing hemicelluloses [23]) formed agglomerated and heterogeneous structures with very poor mechanical integrity, F3 and F3A (consisting of almost pure cellulose [23]) formed more uniform aerogels. The morphology of the aerogels at the micron scale, evaluated by SEM, consisted of fibrillar porous structures, which were indeed much more homogeneous in F3 and F3A. Conversely, larger structures, originated from the native *P. oceanica* cell walls, were detected in F2 and F2A. A higher extent of agglomeration was evident in F2A, giving rise to aerogels with a weaker powder-like consistency. The observed differences were expected due to the higher degree of purification of the F3 and F3A fractions, where cell wall components such as lignin and hemicelluloses had been eliminated. The absence of additional components may facilitate the formation of a strong hydrogen-bonded network of cellulose [23, 25], thus giving rise to aerogels with improved mechanical integrity. Interestingly, the hydrolysis of the cellulosic fractions had a large impact on the morphology and consistency of the obtained nanocellulosic aerogels. In particular, the NANO F3 aerogel (containing pure nanocellulose [23]) presented the most uniform morphology. As shown in the SEM images (cf. Figure 1B), the NANO F2 and NANO F2A aerogels showed the most porous structure, while NANO F3A presented a more compacted structure, where a layer of material coating the surface and reducing the porosity was observed.

As expected, the morphological differences had a significant effect on the density of the aerogels (cf. Table 1). The greater degree of agglomeration and heterogeneity of the F2 and F2A aerogels were also evidenced by their greater density values. On the other hand, in general, the greater porosity and uniformity of the nanocellulosic aerogels resulted in a

marked decrease in their densities with respect to the corresponding cellulosic aerogels. This effect was more obvious in the case of the least purified fractions (with a 6-fold and 9-fold decrease in the case of NANO F2 and NANO F2A, respectively, with respect to the F2 and F2A aerogels). Thus, NANO F2 and NANO F2A yielded the most porous and lightweight aerogels. Surprisingly, the structure of NANO F3A became denser than F3A, as further supported by the corresponding SEM images. As demonstrated by a previous work, a small amount of the lipidic impurities remaining in the F2A and F3A fractions are resistant to the hydrolysis treatment and therefore, they are still present in NANO F2A and NANO F3A. These lipidic compounds were most likely interacting with the hemicelluloses present in NANO F2A; however, the removal of hemicelluloses by the application of a basic treatment in the case of NANO F3A, seemed to promote the release of these lipids, which were then phase-separated from the pure cellulose and formed a layer coating the surface of the aerogel. The same effect has been previously reported for films prepared from aqueous suspensions of NANO F3A [23]. Thus, these lipidic impurities seem to be responsible for the more compacted structure of the aerogel.

The density values of the NANO F2 and NANO F2A aerogels were significantly lower in comparison with those previously reported for aerogels from cotton cellulose nanowhiskers (78 mg/cm^3) prepared at the same concentration (0.5 wt.-%) by solvent exchange and supercritical CO_2 drying [8]. Similar densities were obtained in hybrid nanocellulose aerogels with added carbon nanotubes, achieving values ranging between $10\text{-}56 \text{ mg/cm}^3$ [27]. Lower densities have only been reported for modified cellulose aerogels. For instance, densities of $1.7\text{-}8 \text{ mg/cm}^3$ have been reported for aerogels from rice straw nanofibrils modified by vapour deposition of triethoxyl(octyl) silane [28].

Figure 1. Visual aspect and SEM micrographs from the surface of the *P. oceanica* cellulosic (A) and nanocellulosic (B) aerogels. Scale bars in the SEM micrographs correspond to 1 mm.

Table 1. Density and oil sorption capacity of the *P. oceanica* cellulosic and nanocellulosic aerogels. Different letters show significant differences between samples ($p \leq 0.05$).

	Density (mg/cm ³)	Oil sorption capacity (g oil/g aerogel)
F2	79.4 ± 2.8 ^d	n.m.
F2A	114.3 ± 7.9 ^e	n.m.
F3	42.3 ± 1.3 ^b	20.0 ± 0.1 ^b
F3A	46.8 ± 0.8 ^{bc}	17.4 ± 0.2 ^c
NANO F2	13.2 ± 0.2 ^a	34.3 ± 0.4 ^a
NANO F2A	12.8 ± 0.1 ^a	33.8 ± 0.5 ^a
NANO F3	38.4 ± 0.3 ^b	20.1 ± 0.2 ^b
NANO F3A	58.1 ± 0.2 ^c	12.2 ± 0.2 ^d

To evaluate the effect of the distinct composition and morphology of the aerogels on their sorption capacity, water and oil sorption tests were carried out. Unfortunately, due to the highly hydrophilic character of the (nano)cellulosic aerogels, they disintegrated when immersed in water and therefore, water sorption could not be assessed. The results from the oil sorption tests showed a clear correlation between the porosity and sorption capacity of the aerogels (cf. Table 1). It should be noted that the poor mechanical integrity of the F2 and F2A aerogels impeded reliable results to be obtained from the oil sorption tests and thus, these values have not been reported. The most porous NANO F2 and NANO F2A aerogels presented the highest oil sorption capacity, while the more compacted structures found in NANO F3A limited their performance. Similar sorption values were observed in *A. donax* cellulosic aerogels (10-60 g oil/g aerogel) [6], while lower capacities (18-20 g oil/g aerogel) have been reported for methyltrimethoxysilane-coated cellulose aerogels [29]. As shown in the sorption curves (cf. Figure S1), the oil was absorbed into the aerogels relatively quickly, reaching equilibrium values approximately after 4h. With regards to the oil release, it was noticeable that all the aerogels released almost completely the oil after 3 days. It should be

noted that the most compacted aerogels, especially F2A, displayed the slower oil release kinetics, showing the importance of the aerogel microstructure on the sorption and desorption processes.

Overall, the NANO F2 and NANO F2A aerogels seem to be the most promising materials, given their reduced production costs and environmental impact (as compared to the more purified nanocellulosic fractions), their optimal microstructure in terms of porosity and homogeneity and their lightweight characteristics.

3.2. Production of hydrophobic PLA-coated (nano)cellulosic aerogels

The poor resistance of the (nano)cellulosic aerogels to high humidity conditions would strongly limit their range of applications. A straightforward methodology based on dipping the (nano)cellulosic aerogels in PLA solutions was evaluated for their hydrophobization and the obtained aerogels were characterized to determine the effect of PLA incorporation on their mechanical performance and sorption capacity. To this end, four aerogels were selected: NANO F2 and NANO F2A (the most optimum in terms of microstructure and sorption capacity) and F3 and NANO F3 (the most purified cellulosic and nanocellulosic fractions). The latter ones were selected to assess the effect of the degree of purification and of the cellulose hydrolysis. Furthermore, four different solid concentrations (0.5, 1, 1.5 and 2 wt.-%) were tested to determine the effect of (nano)cellulose concentration on the morphology, sorption capacity and mechanical integrity of the produced aerogels. The visual aspect and representative SEM images from the obtained aerogels, shown in Figure 2, evidenced that, for a given concentration, the NANO F2 and NANO F2A aerogels presented more porous structures. As expected, increasing concentrations of the (nano)cellulosic fractions led to

denser aerogel structures. The density of the aerogels (cf. Table 2) was directly related to their microstructure, being the more porous materials the ones presenting the lowest density values (i.e. NANO F2 and NANO F2A at their lowest concentration).

Figure 2. Visual aspect and SEM micrographs of the selected *P. oceanica* (nano)cellulosic aerogels at four different concentrations. (A) F3, (B) NANO F3, (C) NANO F2A and (D) NANO F2. Scale bars in the SEM micrographs correspond to 1 mm.

Table 2. Density of the selected *P. oceanica* (nano)cellulosic aerogels at the different tested concentrations and of the corresponding PLA-coated (nano)cellulosic aerogels. Different letters show significant differences between the same concentration (column) while * show significant differences between concentrations for the same material ($p \leq 0.05$).

Density (mg/cm ³)	0.5%	1%	1.5%	2%
F3	42.3 ± 1.3 ^b	76.1 ± 2.3 ^{b*}	98.8 ± 2.8 ^{b**}	125.9 ± 5.5 ^{b***}
F3 + PLA	118.4 ± 5.8 ^c	180.6 ± 5.3 ^{c*}	197.6 ± 10.0 ^{c*}	232.9 ± 15.3 ^{c**}

NANO F3	38.4 ± 0.3^b	$73.8 \pm 0.8^{b*}$	$97.5 \pm 1.2^{b**}$	$113.9 \pm 3.7^{b***}$
NANO F3 + PLA	109.6 ± 4.3^c	$177.0 \pm 7.3^{c*}$	$188.3 \pm 1.9^{c*}$	$216.1 \pm 12.5^{c**}$
NANO F2A	12.8 ± 0.1^a	$23.3 \pm 0.5^{a*}$	$35.1 \pm 1.4^{a**}$	$46.8 \pm 1.8^{a***}$
NANO F2A + PLA	41.6 ± 2.9^b	$73.4 \pm 4.5^{b*}$	$91.3 \pm 5.4^{b**}$	$112.3 \pm 6.6^{b***}$
NANO F2	13.2 ± 0.2^a	$25.7 \pm 0.3^{a*}$	$38.3 \pm 0.8^{a**}$	$51.6 \pm 1.7^{a***}$
NANO F2 + PLA	45.5 ± 4.4^b	$77.1 \pm 4.3^{b*}$	$103.3 \pm 6.3^{b**}$	$116.1 \pm 7.3^{b**}$

After dipping the materials into the PLA solutions, the amount of polymer retained by the aerogels was estimated. As deduced from Figure 3, there was a clear tendency of decreasing the PLA incorporation when increasing the (nano)cellulose concentration. Moreover, the less purified aerogels (NANO F2A and NANO F2) were able to retain greater amounts of PLA than the pure cellulose aerogels. Remarkably, NANO F2A and NANO F2 were able to incorporate more than 200% PLA (with regards to their initial weight) when the nanocellulose concentration in the starting aerogels was 0.5-1 wt.-%. These results were consistent with the higher porosity observed in these particular samples (cf. Figure 2). The density values of the obtained PLA-coated (nano)cellulosic aerogels were also estimated and the obtained values are gathered in Table 2. As expected, the incorporation of PLA significantly increased the density of the aerogels, being this effect more remarkable at the lowest (nano)cellulosic concentration (0.5 wt.-%) since the PLA weight gain was greater in that case. The highest absolute density values (110-230 mg/cm³) corresponded to the 2 wt.-% aerogels, which were within the range of those previously reported for bacterial cellulose aerogels reinforced with PLA produced by ethanol precipitation and supercritical CO₂ drying (162 mg/cm³) [30].

Figure 3. Amount of PLA incorporated into the *P. oceanica* (nano)cellulosic aerogels (%) with respect to the initial aerogel weight). Different letters denote significant differences between concentrations for the same aerogel type while * show significant differences between different aerogels at the same concentration ($p \leq 0.05$).

SEM characterization was also carried out to assess the distribution of the PLA phase in the coated (nano)cellulosic aerogels and representative micrographs are shown in Figure 4. As observed, the PLA-coated aerogels presented much more compact and continuous structures than the pristine (nano)cellulosic aerogels. The PLA seemed to be mostly located filling in the pores and also covering the surface of the aerogels in a particular way: PLA created a continuous layer showing a very singular network of micro-holes (diameter $\sim 3 \mu\text{m}$) which were particularly visible in the 1.5% and 2% aerogels (see insets in Figure 4). These micro-holes were most likely originated by the evaporation of chloroform after the PLA dipping process, and therefore they are expected to appear within the PLA-rich regions.

Figure 4. SEM images of the PLA-coated (nano)cellulosic aerogels. (A) F3, (B) NANO F3, (C) NANO F2A and (D) NANO F2. Insets represent regions of the aerogels at higher magnification.

Since PLA is known to possess a more hydrophobic behaviour than cellulose [31, 32], contact angle measurements were performed on selected aerogels to identify the effect of PLA incorporation on the water affinity of the aerogels' surface. The coating of the aerogels with PLA had a dramatic effect; while the original (nano)cellulosic aerogels were not even measurable due to the highly hydrophilic nature of these materials [23], the PLA-coated (nano)cellulosic aerogels presented contact angle values between 100° and 125°. Such values are similar to those reported for PLA films [31] and demonstrate the marked

hydrophobization effect of the PLA dipping method. Interestingly, the most purified fractions (F3 and NANO F3) showed a more hydrophobic behaviour at the lowest (nano)cellulose concentration (0.5 wt.-%), which was most likely due to the greater amount of PLA incorporated, while this was not the case for the less purified fractions (NANO F2A and NANO F2). These results suggest that in the case of the more porous aerogels PLA was preferentially incorporated into the inner region, filling in the pores. On the other hand, there seemed to be an optimum density range (40-50 mg/cm³, cf. Table 2) for which the PLA was capable of filling the internal pores and the excess polymer was distributed coating the surface of the aerogels, therefore maximizing the hydrophobization effect. Indeed, the most purified aerogels (i.e. F3 and NANO F3) at their lowest concentration (0.5%) and the least purified aerogels (i.e. NANO F2A and NANO F2) at their highest concentration (2%), which presented densities within the “optimum range”, showed the maximum contact angle values, ranging from 110 to 130°.

Table 3. Calculated contact angle, water sorption, oil sorption and oil retention capacities for PLA-coated (nano)cellulosic aerogels at their lowest (0.5%) and highest (2%) concentrations. Values followed by different letters are significantly different ($p \leq 0.05$).

	Contact angle (°)	Water sorption capacity (g H ₂ O/g aerogel)	Oil sorption capacity (g oil/g aerogel)	Oil retention capacity (g oil/g aerogel)
F3 0.5% + PLA	124.5 ± 9.9 ^a	3.3 ± 0.1 ^{de}	6.9 ± 0.1 ^f	0.4 ± 0.1 ^d
F3 2% + PLA	100.9 ± 4.6 ^b	2.8 ± 0.1 ^c	5.9 ± 0.1 ^g	3.9 ± 0.5 ^a
NANO F3 0.5% + PLA	127.1 ± 5.6 ^a	3.7 ± 0.2 ^{cd}	8.4 ± 0.1 ^d	1.2 ± 0.2 ^c
NANO F3 2% + PLA	95.2 ± 8.6 ^b	2.9 ± 0.1 ^c	6.1 ± 0.1 ^g	2.4 ± 0.3 ^b

NANO F2A 0.5% + PLA	101.4 ± 5.7^b	6.7 ± 0.1^a	9.2 ± 0.2^c	0.7 ± 0.1^d
NANO F2A 2% + PLA	120.0 ± 3.1^a	4.2 ± 0.1^c	7.6 ± 0.2^c	3.0 ± 0.2^{ab}
NANO F2 0.5% + PLA	107.1 ± 6.5^{ab}	5.3 ± 0.1^b	8.4 ± 0.1^d	0.8 ± 0.2^{cd}
NANO F2 2%+ PLA	112.3 ± 7.0^{ab}	3.8 ± 0.1^c	7.3 ± 0.1^{ef}	2.6 ± 0.3^b

The dramatic changes in the microstructure and water affinity of the aerogels induced by the incorporation of PLA were expected to affect their sorption capacity. Thus, water and oil sorption experiments were carried out on the PLA-coated (nano)cellulosic aerogels. Water sorption curves for all the aerogels could be fitted by a pseudo-first order equation, while a pseudo-second order model worked better for the kinetics of oil sorption (cf. Figure S2). All the kinetic parameters obtained from the fitting are compiled in the supplementary material (cf. Table S1). Although the surface of the PLA-coated (nano)cellulosic aerogels showed a hydrophobic behaviour, as suggested by the contact angle measurements, the aerogels were able to adsorb water while also keeping their integrity (unlike the pure (nano)cellulose aerogels). The results from the water sorption/desorption experiments (cf. Figure S3) show that the sorption and desorption processes were relatively fast (with all the samples reaching equilibrium values in ca. 4 h for the sorption and 4-8 h for the desorption), suggesting weak interactions between water and the structure of the aerogels. The aerogels containing the less purified fractions (NANO F2 and NANO F2A) presented the highest water sorption capacities, reaching values up to ca. 500-700% (cf. Table 3). It should also be noted that, for all the aerogel types, lower (nano)cellulosic concentrations produced higher adsorption capacities. These results can be directly related to the microstructure of the aerogels, i.e. a lower degree of purification and lower (nano)cellulosic concentrations gave rise to more porous structures, which were able to adsorb more water. The PLA-coated (nano)cellulosic

aerogels were clearly more hydrophobic than other biopolymeric aerogels reported in the literature, such as PVA aerogels loaded with cellulose/nanocellulose, which were able to adsorb up to 800% water [7].

Additionally, oil sorption/desorption tests were carried out to determine the sorption capacity of the aerogels in hydrophobic media. The oil sorption process (reaching equilibrium after ca. 1 h) was much faster than the desorption process (with a steep weight decrease after ca. 3 days and reaching equilibrium after 30 days) (cf. Figure S4). The oil release process took place more slowly in comparison with water, which was expected due to its higher viscosity (ca. 0.049 Pa s at 20 °C [33] versus 0.001 Pa s for water) and evaporation temperature. As for the water sorption capacity, the microstructure of the aerogels played a crucial role in their oil sorption capacity. The oil sorption capacity of the PLA-coated aerogels was clearly diminished in comparison with the highly porous pure (nano)cellulosic aerogels, which can be ascribed to the much more compacted structure attained after the PLA dipping process. Amongst all the PLA-coated (nano)cellulosic aerogels, the more porous structures found in the aerogels from less purified fractions and with lower (nano)cellulosic concentrations led to greater oil sorption values. In particular, the porous NANO F2A aerogels were able to adsorb up to ~920% oil, while the more compacted F3 aerogels adsorbed up to ~690% oil. Higher sorption values of 60 g oil/g aerogel have been reported for recycled cellulose aerogels coated with vapour deposition of methyltrimethoxysilane [14]. These materials presented lower densities than the PLA-coated (nano)cellulosic aerogels presented in this work, again supporting the fact that the porous microstructure plays a crucial role in the adsorption capacity of the aerogels. Interestingly, after drying for an extended time (~50

days), a large amount of oil was released from the most porous aerogels, which could be favourable for their re-utilization if used as adsorbent materials. The denser structures present in the more concentrated aerogels (i.e. 2 wt.-% (nano)cellulose) were capable of retaining larger amounts of oil, with a maximum oil retention capacity of 66% (with respect to the initial amount of sorbed oil) for the F3 aerogel. The morphology of the aerogels at the end of the oil desorption experiments (~50 days) was characterized by SEM, showing that their microstructure significantly changed with respect to their native state (cf. Figure S5). A more solid-like structure of the aerogels was displayed after the incorporation of oil. Both the larger pores and the micro-holes formed within the PLA-rich phase were completely filled by the sunflower oil. Additionally, confocal laser scanning microscopy was used to investigate the oil distribution within the PLA-coated aerogels' structure and a sequential imaging of the oil immersion process is shown in Figure 5 for NANO F2A (0.5%) as a representative example. The micrographs of the pristine aerogels showed the reflexion of the monochromatic light at 488 nm on the materials, exhibiting their porous structure. After soaking the samples in stained sunflower oil, a considerable amount of the latter was adsorbed, being homogeneously distributed all along the aerogel matrix. In contrast, after drying the aerogel, most of the oil was released from the structure and the remaining oil droplets were seen to be mainly located at the surface of the PLA phase.

The results indicate that the PLA-coated (nano)cellulosic aerogels were able to adsorb greater amounts of oil than water, which can be explained by the hydrophobic character provided by the PLA phase. The selectivity of the aerogels to preferentially adsorb oil when soaked in water/oil mixtures was visually examined (cf. Figure 5D). It was observed that after

immersed in the liquid mixture, the PLA-coated (nano)cellulosic aerogels barely adsorbed water, while they were able to selectively adsorb sunflower oil when immersed in the water/oil interphase. Moreover, the aerogel integrity was not damaged at all along the process, proving the higher mechanical resistance acquired after the PLA dipping.

Figure 5. (A-C) Confocal microscopy images of the NANO F2A (0.5%) + PLA aerogel during the oil sorption process. (A) pristine PLA-coated (nano)cellulosic aerogel, (B) after oil immersion and (C) after drying for 50 days. Insets represent higher magnification images from selected aerogel regions. (D) Sequence of the aerogel immersion in a water (blue-stained) and oil (red-stained) mixture.

Compression tests were also carried out to evaluate the effect of the distinct microstructure of the aerogels on their mechanical performance, before and after the incorporation of the PLA, and representative compression stress curves are shown in Figure 6, while the stress values corresponding to 60% deformation are listed in Table 4. It should be mentioned that specimens with the exact dimensions required for the compression tests could not be obtained for the NANO F3 0.5% aerogels due to cellulose agglomeration upon freeze-drying in the sample moulds. As observed in Figure 6, none of the tested samples broke when subjected to a maximum stress of 0.2 N/mm². The pure (nano)cellulosic aerogels showed an initial linear stress-strain region, followed by a region where the stress increased more markedly. In general, increasing the (nano)cellulose concentration improved the mechanical performance of the aerogels. Thus, a greater porosity seemed to be directly linked to a poorer mechanical performance of the aerogels. As expected, the incorporation of PLA substantially increased the compression resistance of all the aerogels, with up to 10-fold improved performance. These results were in agreement with those obtained for nanocellulosic aerogels chemically cross-linked with nanoparticles obtained by freeze-drying (0.01 and 0.05 N/mm²) [34] or those from recycled cellulose aerogels (~0.06 N/mm² for a concentration of 2 wt.-% cellulose) [15].

Noticeably, some of the PLA-coated aerogels displayed a biphasic behaviour. Interestingly, this biphasic behaviour was especially prominent for those aerogels whose density (before PLA coating) ranged between 40-50 mg/cm³. As previously commented, it seems that the porous structures formed within this particular density range allowed the incorporation of PLA within the inner aerogel pores and the excess material was also located coating the surface of the aerogels. Thus, the more marked initial slope detected in the aerogels with

biphasic behaviour was originated by the PLA surface domains. This is in agreement with the SEM characterization, which showed the preferential distribution of the PLA phase filling in the pores of the aerogels and coating the external layers, i.e. no intimate interactions between the cellulose and PLA phase seemed to take place.

Figure 6. Compression stress curves of selected pure (nano)cellulosic aerogels and their respective PLA-coated counterparts.

Table 4. Compressive stress of the selected aerogels with and without PLA-coating at 60% strain. Different letters show significant differences between samples within the same

column. * shows significant differences between the pure (nano)cellulosic aerogels and their respective PLA-coated counterparts. ($p \leq 0.05$).

Compressive Stress (N/mm²)	Pure (nano)cellulosic aerogel	PLA-coated aerogel
F3 0.5%	1.9 ± 0.1^b	$15.1 \pm 0.3^{d*}$
F3 2%	2.0 ± 0.1^b	$16.5 \pm 0.2^{d*}$
NANO F3 0.5%	---	---
NANO F3 2%	5.8 ± 0.5^c	$15.5 \pm 1.4^{cd*}$
NANO F2A 0.5%	0.5 ± 0.1^a	$4.8 \pm 0.2^{a*}$
NANO F2A 2%	3.1 ± 0.3^b	$6.6 \pm 0.1^{b*}$
NANO F2 0.5%	1.9 ± 0.4^b	$12.5 \pm 0.5^{c*}$
NANO F2 2%	2.5 ± 0.6^b	$18.8 \pm 3.1^{d*}$

4. Conclusions

Posidonia oceanica waste biomass has been valorised for the development of lightweight, hydrophobic cellulose-based adsorbent aerogels. Initially, several (nano)cellulosic fractions with different degrees of purification were extracted and used to produce aerogels by freeze-drying. The least purified nanocellulosic fractions (NANO F2 and NANO F2A) gave rise to more porous and lightweight aerogels, capable of adsorbing greater amounts of oil (~34 g oil/g aerogel). However, all the produced aerogels showed very poor performance in high humidity conditions.

The most promising aerogels (NANO F2 and NANO F2A), together with the pure cellulose-based aerogels (F3 and NANO F3), were subsequently subjected to a simple PLA dipping method to hydrophobize their surface, producing PLA-coated (nano)cellulosic aerogels. The concentration of (nano)cellulose in the starting aerogels had a strong impact on their

microstructure: more porous aerogels, capable of incorporating greater amounts of PLA into their structures, were obtained with lower (nano)cellulose concentrations. PLA incorporation led to surface hydrophobization, with all the coated aerogels presenting contact angles of 95-130° and being able to keep their integrity when soaked in water. These PLA-coated (nano)cellulosic aerogels were capable of selectively adsorbing greater amounts of oil (5.9-9.2 g oil/g aerogel) than water (2.8-6.7 g H₂O/g aerogel). The sorption capacity of the aerogels was correlated with their microstructure, with the most porous materials being more susceptible to the sorption/desorption of liquid media. The incorporation of PLA led to a substantial increase on the compression stress (up to 10-fold) of the coated aerogels. Moreover, the mechanical performance was also strongly related to the microstructure, being a greater porosity linked to poorer mechanical performance. Overall, the aerogels' microstructure plays a crucial role on their properties, before and after PLA coating.

These results show that the least purified fractions from *Posidonia oceanica* waste biomass have a great potential to develop fully bio-based, extremely lightweight, hydrophobic and highly adsorbent aerogels with good mechanical properties by using a simple PLA dipping method. These materials represent a greener and more sustainable alternative for the development of adsorbent structures useful in diverse applications, such as oil spill cleaning and food packaging.

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Supplementary Material

Additional Supplementary Material may be found in the online version of this article.

Figure S1. Oil sorption and desorption kinetics for the *P. oceanica* (nano)cellulosic aerogels (0.5 wt.-%).

Figure S2. Fitting of the oil and water sorption kinetics for the NANO F2A 0.5% + PLA aerogel using pseudo-first order and pseudo-second order models.

Figure S3. Water sorption/desorption kinetics of the different aerogels at their different concentrations.

Figure S4. Oil sorption/desorption kinetics of the different aerogels at their different concentrations.

Figure S5. SEM images of selected PLA-coated (nano)cellulosic aerogels after the oil desorption experiments.

Table S1. Kinetic parameters obtained by fitting the oil and water sorption curves to pseudo-first order and pseudo-second order models.

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Supplementary material

Figure S1. Oil sorption (A) and desorption (B) kinetics for the *P. oceanica* (nano)cellulosic aerogels (0.5 wt.-%).

Figure S2. Oil (A) and water (B) sorption kinetics for the NANO F2A 0.5% + PLA aerogel. The dotted lines correspond to the fitting curves obtained using pseudo-first order and pseudo-second order models.

Table S1. Kinetic parameters obtained by fitting the oil and water sorption curves to pseudo-first order and pseudo-second order models.

	OIL			WATER		
	q_e (%)	k_2	R^2	q_e (%)	k_1	R^2
F3 0.5% + PLA	686.7	$3.4 \cdot 10^{-4}$	0.9980	305.8	$4.3 \cdot 10^{-4}$	0.9837
F3 1% + PLA	627.1	$1.7 \cdot 10^{-4}$	0.9994	288.2	$7.0 \cdot 10^{-5}$	0.9207
F3 1.5% + PLA	639.5	$3.8 \cdot 10^{-4}$	0.9969	291.5	$7.7 \cdot 10^{-5}$	0.9597
F3 2% + PLA	583.8	$1.1 \cdot 10^{-3}$	0.9996	260.4	$1.7 \cdot 10^{-4}$	0.9735
NANO F3 0.5% + PLA	835.5	$6.7 \cdot 10^{-4}$	0.9997	355.9	$7.3 \cdot 10^{-5}$	0.9942
NANO F3 1% + PLA	804.8	$3.7 \cdot 10^{-3}$	0.9985	321.5	$6.5 \cdot 10^{-5}$	0.9916
NANO F3 1.5% + PLA	641.3	$9.7 \cdot 10^{-4}$	0.9937	294.1	$9.4 \cdot 10^{-5}$	0.9856
NANO F3 2% + PLA	594.8	$8.2 \cdot 10^{-4}$	0.9986	274.0	$1.9 \cdot 10^{-4}$	0.9843
NANO F2A 0.5% + PLA	942.6	$7.4 \cdot 10^{-4}$	0.9987	699.3	$2.3 \cdot 10^{-5}$	0.9733
NANO F2A 1% + PLA	788.7	$4.1 \cdot 10^{-4}$	0.9962	584.8	$2.7 \cdot 10^{-5}$	0.9746
NANO F2A 1.5% + PLA	730.6	$5.4 \cdot 10^{-3}$	0.9994	456.6	$5.9 \cdot 10^{-5}$	0.9863
NANO F2A 2% + PLA	745.8	$1.7 \cdot 10^{-3}$	0.9992	458.7	$3.3 \cdot 10^{-5}$	0.9575
NANO F2 0.5% + PLA	836.7	$2.0 \cdot 10^{-4}$	0.9987	531.9	$4.1 \cdot 10^{-5}$	0.9936
NANO F2 1% + PLA	771.7	$3.7 \cdot 10^{-4}$	0.9975	401.6	$3.2 \cdot 10^{-5}$	0.9673
NANO F2 1.5% + PLA	748.7	$3.1 \cdot 10^{-3}$	0.9991	369.0	$5.7 \cdot 10^{-5}$	0.9226
NANO F2 2%+ PLA	722.9	$4.0 \cdot 10^{-3}$	0.9996	371.7	$3.9 \cdot 10^{-5}$	0.9642

A

B

C

Figure S3. Water sorption/desorption kinetics of the different aerogels at their different concentrations (0.5-2%) being (A) F3, (B) NANO F3, (C) NANO F2A and (D) NANO F2.

A

C

Figure S4. Oil sorption/desorption kinetics of the different aerogels at their different concentrations (0.5-2%) being (A) F3 (F), (B) NANO F3, (C) NANO F2A and (D) NANO F2.

Figure S5. SEM images of the selected PLA-coated (nano)cellulosic aerogels after the oil desorption experiments. (A) corresponds to NANO F2 0.5% and (B) to NANO F2 2%.