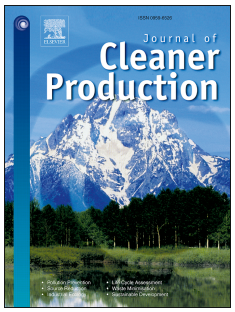

Up-cycling coffee silverskin into biobased functional coatings

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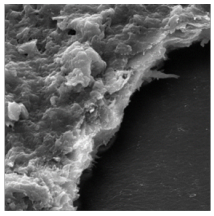
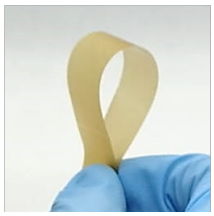
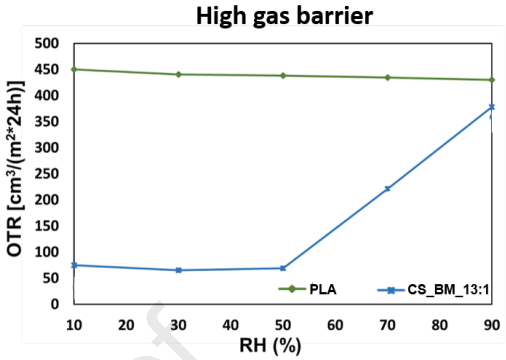


CS based coatings





Up-cycling coffee silverskin into biobased functional coatings

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Abstract

In this work, a novel route for the up-cycling of coffee silverskin (CS) based on a sustainable mechano-chemical process has been developed. CS was treated in a planetary ball milling in presence of water and the resulting suspension was used to realize thin bio-coatings deposited onto flexible packaging polylactic acid (PLA) films. CS based coatings exhibit homogeneous morphology, excellent adhesion on PLA substrates and good flexibility. The coatings display UV blocking properties, reducing the UV transmittance of PLA in the range 200-400 nm to values as low as 0.34%-2.67%, depending on the coating thickness and the process conditions. Moreover, a significant improvement of the oxygen permeability barrier has been also recorded; CS coated films show an O_2 transmission rate reduction up to 91% at 25 °C and 50% relative humidity with respect to PLA.

Keywords

Agricultural waste; Biomass; Waste-to-resource; Ball milling; Functional packaging; Circular Economy

1. Introduction

Coffee silverskin (CS) is a strongly adherent layer that directly envelops the green coffee bean. Its detachment occurs during roasting due to the physical expansion of the beans, resulting in a major by-product of coffee production (Gottstein et al., 2021). It has been estimated that about 400 thousand tonnes of CS is generated each year by the coffee roasting industry. Recently, different approaches to the valorization of coffee industry byproducts and, in particular, of CS have been suggested (Nolasco et al., 2022a), attempting to address sustainability issues implementing a circular economy approach. Indeed, the valorization of byproducts deriving from the food industry, aiming at reducing waste production and maximizing the efficiency of food value chains is an important challenge and a key objective to move towards the circularization of economy.

On one hand, many research groups have been focusing on the utilization of coffee wastes in foods as source of sugars, minerals and fibers (Mussatto et al., 2011; Nolasco et al., 2022b), alternative renewable energy sources like bio-diesel oil and bio-ethanol (Kondamudi et al., 2008; Al-Hamamre et al., 2012), electrode materials, soil fertilization, and cosmetic application (Bessada, 2018). Biopolymers such as polyhydroxyalkanoates can be also produced from the oil fraction of spent coffee grounds or by the hydrolysis and fermentation of the carbohydrates contained in coffee wastes (Saratale et al., 2021). On the other hand, many studies on the utilization of coffee by-products as filler/reinforcement in polymeric composite materials have been carried out, based on different “traditional” polymers like (bio)polyethylene (Dominici et al., 2019) and polypropylene (Zarrinbakhsh et al., 2016) but also on bio-polyesters (Ghazvini et al., 2022). Spent coffee grounds and coffee silverskin have been employed, often after proper chemical functionalization, to enhance the thermal or mechanical properties of the polymer matrices, and to promote UV-blocking, antimicrobial or antioxidant properties into the composite. For example, CS was embedded as a reinforcing agent in poly(butylene adipate-co-terephthalate)/poly(3-hydroxybutyrate-co-valerate) (PBAT/PHBV) composites: polyphenols extracted and silane-modified CS provided the best combination of resistance properties and ductility, compared to untreated CS (Sarasini et al., 2018a). However, untreated CS induced increased thermal stability and antioxidant activity in the same polymer blends (Sarasini et al., 2018b), evidencing a trade-off between the incorporation of antioxidant-rich CS and the optimization of the mechanical properties of the composites. With another approach, films based on potato starch, glycerol and untreated coffee silverskin have been developed and proposed for active food packaging: the ability of the CS active constituents to migrate in the aqueous phase during the gelatinization of the films was exploited to develop films with antioxidant and UV-protection features (Oliveira et al., 2020).

The combination of biobased and biodegradable polymers with biobased functional additives represents a step towards the development of sustainable formulations, able to compete with petroleum-based

materials guaranteeing the same performances and functionalities (Oliveira et al., 2021), in the frame of a circular economy approach. An increased use of biobased polymers in the plastic markets is indeed seen as a key strategy to reduce the consumption of fossil carbon sources and to mitigate the environmental impact of plastics, in particular concerning their end of life (European Bioplastics e.V., n.d.; Suarez et al., 2022). At the European level, the European Green Deal and new circular economy action plan has been developed, in which the European Commission announced a policy framework for the regulation of the sourcing, labelling and use of bio-based, biodegradable and compostable plastics ("Biobased, biodegradable and compostable plastics," n.d.). Polylactic acid (PLA) is one of the most commonly used bioplastic (Avella et al., 2009) which, nevertheless, has low thermal stability and poor water vapor and gas barrier properties (Sanchez-Garcia and Lagaron, 2010) if compared, for instance, to other benchmark packaging polymers such as polyolefins and polyethylene terephthalate (PET). These facts are limiting the application of PLA in the packaging sector, where gas barrier properties are a fundamental objective in order to guarantee high quality and safety of foods, considering that oxygen is involved in most food degradation processes. Most commercial solutions to improve the barrier properties of polymer films rely on the realization of multilayer structures containing metal layers (vacuum deposited aluminum or laminated aluminum foil) or high barrier synthetic polymers, such as poly(vinyl alcohol). These kind of solutions, while offering a high protective function, are obviously an issue for the recycling or the biodegradation/composting of the materials, so that their application to bioplastic packaging solutions is no longer sustainable. To ensure circularity and sustainability of plastics and plastic packaging, their end of life must be taken into account in all design steps (Guerritore et al., 2022), significantly reducing the complexity of packaging products and decreasing the amount of non-recyclable fractions, including barrier layers and coatings. In this respect, in recent years, a number of environmentally-friendly, high barrier solutions have been proposed, aiming at the realization of films and coatings based on natural, biodegradable or even edible materials (Lin and Zhao, 2007). Coatings based on natural, biodegradable materials such as lipids, polysaccharides (Cazón et al., 2017), proteins (Chen et al., 2019) and their combination (Benbettaïeb et al., 2016), can provide both moisture and gas barrier properties. In particular, highly polar polymers, such as proteins and polysaccharides are largely exploited since their extensive hydrogen bond networks result in extremely low gas permeability values, especially at low relative humidity (RH) (Baldwin et al., 2011).

Here, fully biobased coatings have been obtained from coffee silverskin by a mechano-chemical (Baláž et al., 2013) treatment carried out in a planetary ball mill (BM), in the presence of water as solvent/dispersing medium. The obtained suspensions have been deposited onto PLA substrates, demonstrating strong beneficial effects on the barrier properties of PLA and thus showing good potential for the development of renewable and sustainable packaging materials. The deposition was realized without any additive, relying only on the self-assembly of CS components, particularly proteins and cellulosic particles (Martuscelli et al.,

2021; Nolasco et al., 2022a) upon drying for the formation of the coatings. Solvent- and water-based coatings are used in the polymer film industry for various aims, such as adhesives and inks, or to confer antistatic, barrier and specific optical properties (Gutoff and Cohen, 2016). Such coatings can be deposited onto polymer films by means of high throughput technologies based on, as an example, variations of the roll coating or slot coating concepts (Gutoff and Cohen; 2016, Schiessl et al., 2023). Bio-based coatings, essentially based on water suspensions of cellulose, are attracting increasing interest due to their good barrier properties and have been proposed for different substrates, including PET (Fotie et al., 2023) and PLA (Meriçer et al., 2016). However, to the best of our knowledge, there are no previously published reports on the development of CS based coatings. Ball milling treatments have been proposed and widely experimented as a green, effective physical method for the deconstruction of the complex, hierarchical structure of cellulose (Avolio et al., 2012) and lignocellulosic biomasses (Pang et al., 2019), a necessary step for the recovery and valorization of their constituents (cellulose and other polysaccharides, lignins, proteins, bioactive and functional compounds). In particular, BM carried out in the presence of water (wet BM) has been shown to efficiently disrupt lignocellulosic materials down to sub-micrometric particle size (Vaidya et al., 2016). Water plays a major role in the process as it favors swelling and, by interacting with the highly hydrophilic constituents of the biomass, weakens the H-bond network between cellulosic fibers, lignins and the other components and intercalates between them, allowing to disrupt the secondary structures (that are mostly based on hydrogen bond networks). Water is also crucial in extracting the soluble fractions and, by hydrating particle surface, in stabilizing the suspensions during milling, avoiding reaggregation (Sitotaw et al., 2023).

After BM, CS suspensions were directly deposited onto PLA substrates without any further treatment. The materials obtained showed a good adhesion to the substrate, interesting morphology and a good barrier to UV-vis radiation and oxygen, demonstrating an innovative strategy for the realization of biobased coatings by the integral recovery of agricultural byproducts.

2. Materials and Methods

2.1. Materials

Coffee silverskin was kindly supplied by local coffee roasting plants, as a byproduct of their process.

Poly (lactic acid) film, thickness 40 µm, corona treated with a surface tension > 38 dyne/cm, was kindly supplied by Flex Packaging AL S.p.A. (Cava de' Tirreni, Italy).

2.2. Ball Milling Treatment

Coffee silverskin samples were processed in a Retsch PM100 planetary ball milling system (Haan, Germany) in wet conditions, using a 125 mL zirconia milling cup and 10 mm zirconia spheres. The BM treatments were

carried out using a spinning speed of 300 rpm, a spheres/dry CS weight ratio of 25:1 and a total milling time of 6 hours. Three different water/CS ratios were tested: 3 g of CS were added in the milling cup with 30 mL, 40 mL or 60 mL of distilled water and the mixture was ball-milled. The milling parameters were selected based on our experience with the BM of agricultural biomasses and of optimization trials. We established the minimum and maximum water/CS ratio resulting in homogeneous suspensions with reasonable viscosity. In fact, with a too low water/CS ratio, the material during milling became too viscous, hindering the movement of grinding balls an, then, the milling action; a too large water/CS ratio also lowers the effectiveness of the balls resulting in an incomplete milling due to excessive dilution of the solid fraction and low viscosity. We also optimized the filling level, avoiding an overfilling at the highest amount of water, and selected the milling speed to keep heating effects at a minimum (the temperature measured immediately after milling did not exceed 40 °C).

The processed CS suspensions were coded as CS_BM_X, where X indicates the water/CS weight ratio, namely 10:1, 13:1, 20:1.

For further analyses, CS_BM_X samples were centrifuged for 15 minutes, at 10°C and 13000 rpm, in order to separate the supernatant and the precipitate fraction, coded as CS_BM_X_S and CS_BM_X_P, respectively.

2.3. Coatings Realization

CS_BM_X suspensions obtained by BM treatments were recovered and directly deposited onto PLA films, without any further refinement or processing. The deposition was carried out by rod coating ("K hand coater", Royston, United Kingdom), using different rods to adjust the amount of material deposited, and covering an area of approximately 10 x 18 cm (Figure 3). Dry CS based coatings were obtained after water evaporation at room temperature (25°C and 50% RH, 2 h). In particular, coating rods with threads of 50 µm and 100 µm were used to deposit the CS suspension obtained with the water/CS weight ratios 10:1 and 13:1; coating rods with threads of 50 µm, 100 µm and 200 µm were used with the more diluted CS suspension (water/CS = 20:1). These conditions allowed to obtain coatings with nominal thickness ranging from 1.5 µm to 5.8 µm (Table 1). These values were evaluated assuming that the density of the coating can be approximated by that of cellulose, which is its main constituent (Nolasco et al., 2022a; Daicho et al., 2020).

Table 1. Nominal thickness of the CS coatings

Water/CS weight ratio	Coating thickness (µm)		
10:1	2.8	5.6	-
13:1	2.1	4.3	-

20:1	1.5	2.9	5.8

Coated PLA films were coded as CS_BM_X_Y where Y indicates the nominal thickness in µm of the coating.

2.4. Characterization

Fourier transform infrared spectra were collected on untreated CS, on dried BM samples (CS_BM_X) and the respective supernatant fractions CS_BM_X_S, by means of a Perkin Elmer Spectrum One FTIR spectrometer (Perkin Elmer Inc., USA), equipped with an attenuated total reflectance accessory (ATR). Spectra were recorded using a resolution of 4 cm^{-1} and 32 scans, in the 4000-650 cm^{-1} range. ATR-FTIR analyses were carried out on CS_BM_X and CS_BM_X_S free standing films, obtained by deposition of the ball milled suspensions onto PTFE substrates followed by water evaporation.

^{1}H NMR spectra were recorded on CS_BM_X_S samples (water soluble fractions) by means of a 600 MHz Bruker Avance III 600 spectrometer, equipped with a 5-mm CPTCI CryoProbe. An excitation sculpting pulse sequence was used to strongly reduce the intensity of water resonance.

Scanning electron microscopy (SEM) analysis was carried out with a FEI Quanta 200 FEG SEM (Thermo Fisher Scientific Inc., USA) in high vacuum mode (about 10^{-5} mbar), using a secondary electron detector and an acceleration voltage of 10–30 kV. The morphological characterization was performed on the coated PLA films (CS_BM_X_Y) surfaces and on the BM suspensions (CS_BM_X). CS_BM_X_Y samples were prepared by cutting square specimens (approximately 8 x 8 mm) by means of a surgical scalpel blade, then each specimen was attached onto an aluminum stub covered with an electrically conductive adhesive disk. Broken/detached portions of CS coating were formed at the edges during cutting, allowing a direct observation of their cross section. CS_BM_X suspensions specimens were pre-diluted (1:50) with distilled water, deposited onto aluminum SEM stubs and dried at room temperature. Before the analysis, samples were sputter coated with gold/palladium by means of an Emitech K575X sputter coater (operating pressure 10^{-2} mbar).

Image analysis for the determination of particle size distribution was carried out on high magnification SEM micrographs using the free software ImageJ. The images were processed by adjusting contrast and transformed in black/white images, then particles and their geometrical parameters were identified using the built-in function of the software. The dimension of each particle was expressed as equivalent diameter, that is, the diameter of a circle with the same area.

Bright field transmission electron microscopy (TEM) analysis of CS_BM_X and CS_BM_X_S was performed by using a FEI Tecnai G12 Spirit Twin (LaB6 source) apparatus (Thermo Fisher Scientific Inc., USA) operating at about 10^{-7} mbar and with 120 kV acceleration voltage. TEM images were collected on a FEI Eagle 4k CCD

camera. Before the analysis, CS_BM_X and CS_BM_X_S were properly diluted with distilled water; samples were collected by immersing TEM copper grids in the aqueous dispersions.

UV–visible spectra were recorded on PLA coated films (CS_BM_X_Y) and neat PLA film by means of a V570 UV spectrophotometer (Jasco, Easton, PA, USA) in the range 200–800 nm. The transmittance was measured by placing the specimens vertically in sample holders placed at 5 cm distance from the light source.

Oxygen transmission rate measurements were performed on PLA coated films (CS_BM_X_Y) and neat PLA film using a PermO2 Extrasolution Permeabilimeter (PermTech, Pieve Fosciana, Italy) at 25 °C and 50% RH. Permeability values were then obtained by normalizing the OTR values for the overall thickness and oxygen pressure gradient across the film (1 bar). To estimate the oxygen permeability of the CS coating alone, knowing the thickness and the permeability of the PLA substrate, a calculation based on a "series resistance" model can be applied (Benbettaieb et al., 2023, Božović et al., 2023), resulting in the following formula:

$OP_{CS} = l_{CS}/[(l_{PLA+CS}/OP_{PLA+CS})-(l_{PLA}/OP_{PLA})]$

Where OP_{CS} , OP_{PLA} and OP_{PLA+CS} represent the oxygen permeability of the CS coating alone, of the PLA substrate and of the PLA + CS coated film, respectively, and l_{CS}, l_{PLA} and l_{PLA+CS} are the thickness of the CS coating alone, of the PLA substrate and of the PLA + CS coated film, respectively.

A further investigation at variable relative humidity, increasing RH of 10% from 10% to 90% was performed on CS_BM_13:1_Y films. The film were tested progressively from the lowest (10%) to the highest (90%) humidity conditions and after completing the 9 measurements, all samples were tested a second time at 50% RH, in order to assess the stability of the CS coatings barrier properties upon exposure to high RH.

3. Results and Discussion

3.1. Ball-Milled Coffee Silverskin

The effects of the mechano-chemical treatment on the chemical structure and morphology of coffee silverskin were investigated by means of ATR-FTIR and SEM analyses. It is known, in fact, that intensive BM treatments can induce, besides the discussed morphological modifications, also chemical reactions including the cleavage of covalent bonds and the formation of radicals (Kwiczak-Yiğitbaşı et al., 2020), oxidation (Kiani et al., 2022), and scission of polymeric chains (Zhou et al., 2023). Although chemical modifications are not the goal of our treatments, their occurrence cannot be excluded *a priori*. In Figure 1, ATR FT-IR spectra of ball-milled materials (CS_BM_10:1, CS_BM_13:1, CS_BM_20:1) and untreated CS are shown. As widely reported in literature, from a compositional point of view CS is a complex mixture in which carbohydrates (essentially cellulose and hemicellulose), and proteins are the main components (Nolasco et al., 2022b) besides lignin, fatty acids, polyphenols, minerals and minor organic/inorganic substances (Ballesteros et al., 2014; Iriondo-DeHond et al., 2019). The main peaks observed in the FTIR

spectra appear rather broad, due to the overlapping of the absorbance of the same functional groups present in different components of CS, thus reflecting its heterogeneous composition.

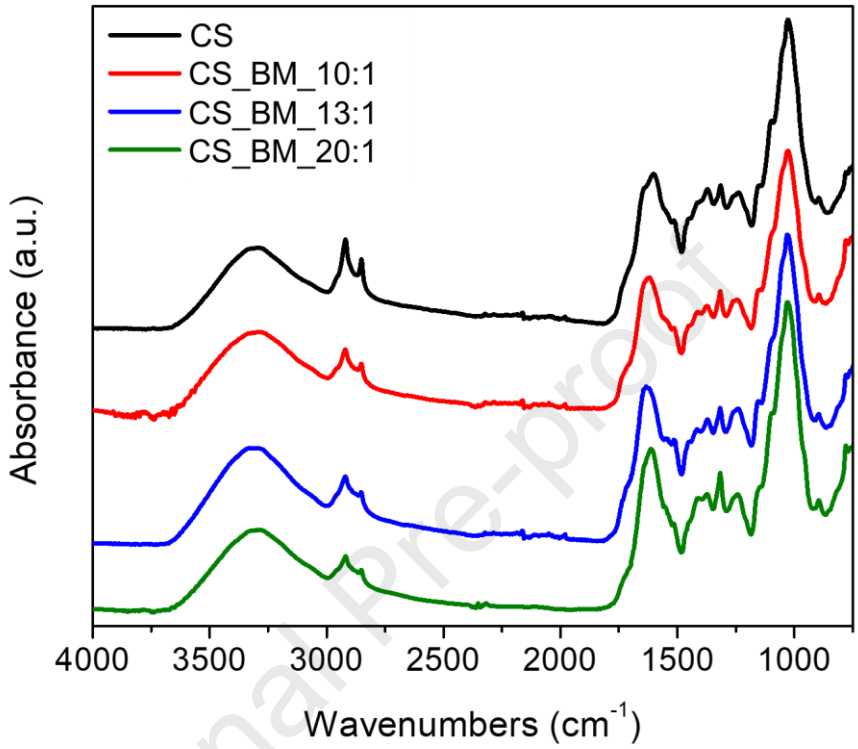

Figure 1. ATR-FTIR spectra of CS and ball-milled CS.

The main absorptions bands can be assigned as (Agudelo-Cuartas et al., 2021; Pancholi et al., 2023; Zarrinbakhsh et al., 2016):

- a very broad band centred at 3300 cm^{-1}, assigned to the stretching of OH (lignin, polysaccharides) and NH (peptides, proteins);

- the asymmetric and symmetric CH stretching signals in the 2920 cm^{-1} – 2850 cm^{-1} range;

- a complex peak in the carbonyl region, with a main band centred at 1640 cm^{-1} assigned to amide (peptide) carbonyls and a shoulder at higher wavenumbers, indicating other carbonyl/carboxyl-containing compounds;

- multiple peaks in the 1500 − 1200 cm^{-1} range, that can be correlated to C−N and C−O stretch, C−N−H and C−O−H bend;

- an intense complex band centred at 1030 cm^{-1}, typical of polysaccharides, and related to the C–O stretching and the CH rocking vibrations.

Comparing the spectra of ball-milled and untreated CS, no relevant changes can be observed suggesting that the ball milling process does not induce any relevant chemical modification, at least in the most abundant components of CS.

In Figure 2, SEM micrographs of untreated and ball-milled CS materials (CS_BM_13:1) are shown. A set of SEM micrographs of all ball milled samples is reported in Figure S1 and S2, and the particle size distribution calculated from SEM micrographs is reported for each water:BM ratio in Figure S3 in the Supplementary file. The morphology of neat CS is mainly characterized by fibrous, irregular particles, with lateral dimension up to 1 mm and a wide range of thicknesses (Figure 2a). At higher magnification, these fibrous structures appear composed by a complex aggregation of fiber-like formations, with smaller globular particles appearing at the surface (Figure 2b-c). As a result of the ball milling treatment, a profound destructuration and fragmentation of the fibrous structures of CS was obtained. The ball-milled suspensions during drying onto the stubs underwent some self-assembly, forming clusters of sub-micrometric particles (Figure 2e, Figure S1) and showing the presence of some residual fibrous formation (Figure 2d, Figure S2). At higher magnification, it was possible to identify the primary CS particles (Figure 2f, Figure S1 b, d, f) as spherical/globular particles with size ranging from about 20 nm to hundreds of nm, similar for all compositions. Image analysis of the high magnification SEM micrographs confirmed this observations, revealing that in all samples more than 50% of particles have an equivalent diameter of less than 40 nm and more than 75% have an equivalent diameter of less than 60 nm. The “fine fraction” below 60 nm is slightly higher at the highest water:CS ratio.

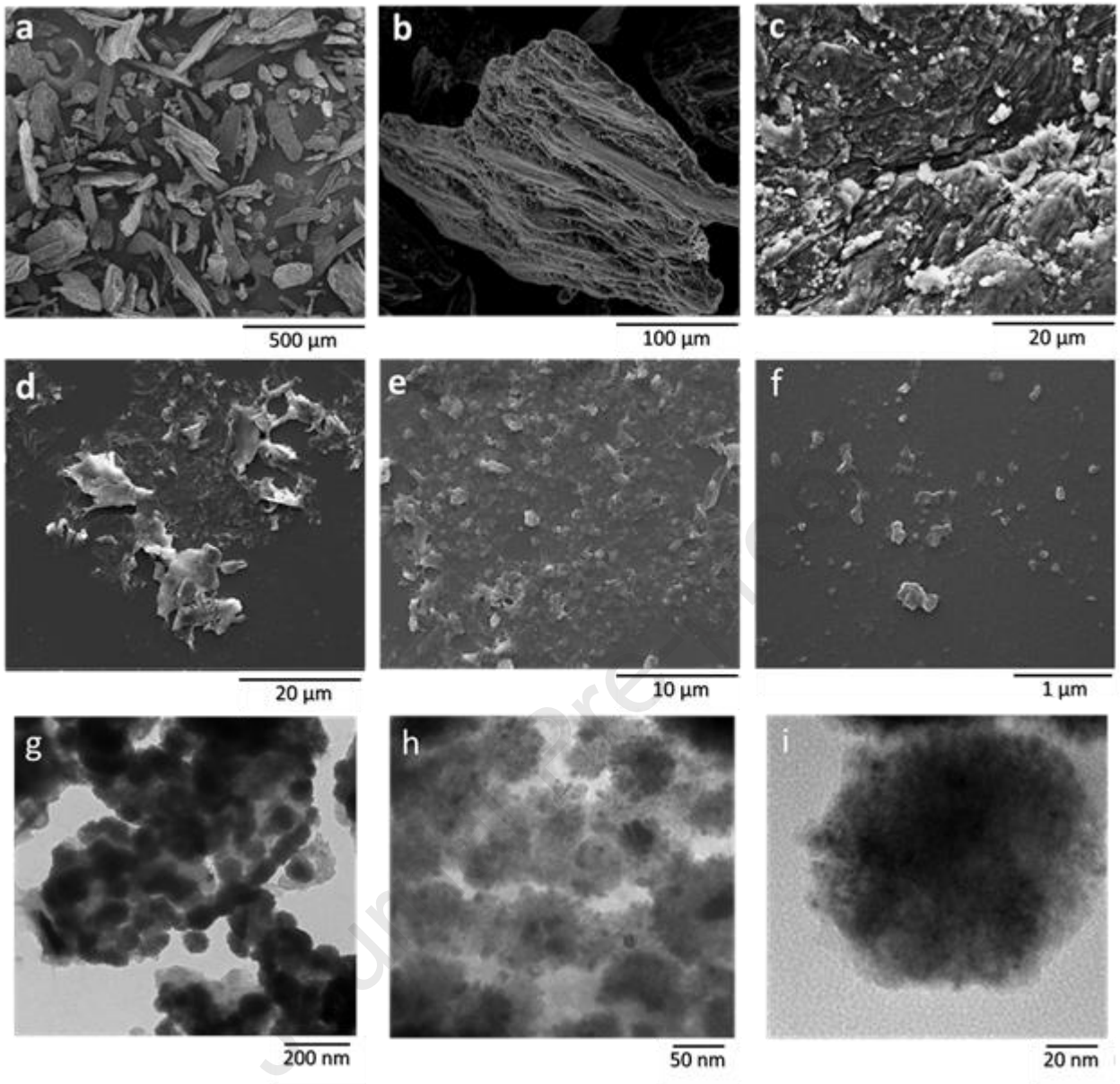

Figure 2. SEM micrographs of untreated CS (a, b, c) and ball-milled samples CS_BM_13:1 (d, e, f); TEM micrographs of CS_BM_13:1 (g, h, i).

TEM analysis (Figure 2 g, h, i) further confirmed that the mechanical destructuration of CS led mainly to the formation of sub-micrometric primary particles, with size ranging from few tens to few hundreds of nm.

3.2. Coffee Silverskin Coatings: Morphology and Structure

The ball-milled CS suspensions were deposited onto commercial PLA flexible packaging films to explore the possibility to realize fully bio-based gas barrier coatings. Coatings with thickness ranging from 1.5 µm to 5.8 µm, as a function of the concentration of the suspension and of rod coater selected for the deposition, were obtained from BM_CS_X samples. Coated films are translucent and show a light-brown coloration,

proportional to coating thickness, as a consequence of the native colour of CS; all coatings show an excellent adhesion to the PLA substrate, withstanding without damage mechanical stress such as the bending of the films. The appearance of all coated films is reported in Figure 3.

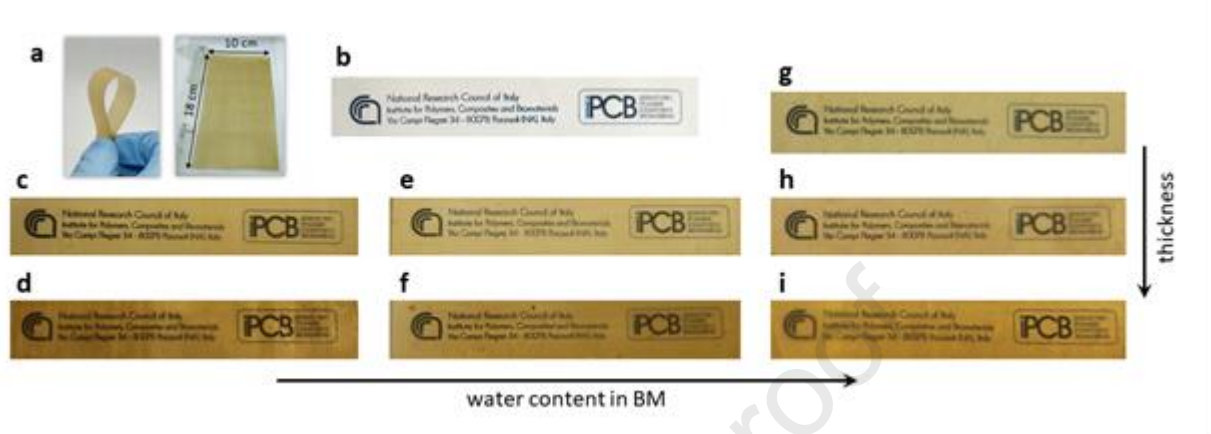

Figure 3. Pictures of CS coated PLA films showing the flexibility of the coating and the large area (10x18 cm) covered by the coating CS_BM_13:1_2.1 (a), image of text printed on white paper (b) and covered with CS coated PLA films: CS_BM_10:1_2.8 (c), CS_BM_10:1_5.6 (d), CS_BM_13:1_2.1 (e), CS_BM_13:1_4.3 (f), CS_BM_20:1_1.5 (g), CS_BM_20:1_2.9 (h), CS_BM_20:1_5.8 (i).

From a morphological point of view, all CS coatings appear as homogeneous, continuous and compact layers composed by a stacking of micrometric and sub-micrometric globular particles, as evidenced by SEM micrographs of surfaces and cross-sections reported in Figure 4. At the lowest water content (sample CS_BM_10:1, Figure 4a-d), the coating surface appears smoother than the other samples, that is, less particles are shown at the surface, probably due to an influence of water content on the drying process (further discussed in Section 3.3). Nevertheless, for all samples, at higher SEM magnification, the main features observed are spherical particles sized in the range of tens to hundreds of nm, apparently embedded in a continuous phase (Figure 4 c,g,k), confirming a composite nature of the CS_BM films. These features are common for all films realized, regardless of their thickness, therefore, for the sake of simplicity, SEM images of only one film for each formulation were reported.

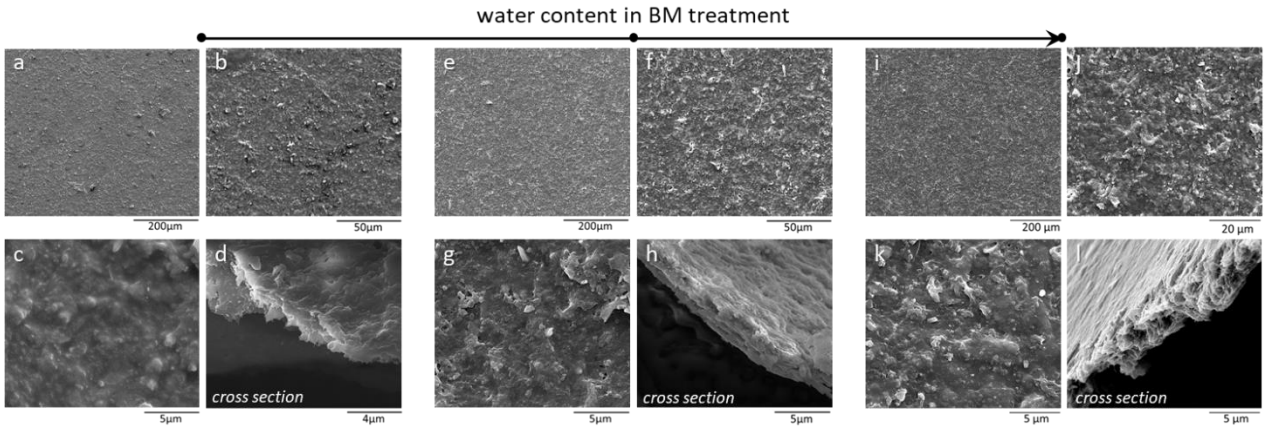

Figure 4. SEM images of coatings CS_BM_10:1_2.8 (a- d); CS_BM_13:1_2.1 (e-h) and CS_BM_20:1_2.9 (i-l).

Trying to clarify the film forming ability of the coffee silverskin, in relation to its composition and to the BM treatment, water soluble and insoluble fractions of ball-milled CS were separated and recovered as detailed in the experimental section. TEM analysis performed on the soluble fraction evidenced its film forming ability. In fact, after water evaporation, a homogeneous and continuous film was formed in which no particle-like structures can be observed, as shown in the Supplementary file, Figure S4. On the contrary, large clusters of particles define the morphology of the unsoluble fraction whose aggregation, induced by the centrifugation process, prevented redispersion. On the basis of these evidences, the film forming ability of ball-milled CS can be ascribed to the soluble fraction components which act as binder phase incorporating the heterogeneous particle-like structures of CS.

To gather more information on the composition of this soluble fraction, ATR FT-IR spectra were recorded on dried CS_BM_X_S samples and compared to the spectra of CS_BM_X (Figure S5 in the Supplementary file). An increased relative intensity of the band at about 1500 cm^{-1}, and of the strong signal centred at about 1600 cm^{-1}, can be evidenced in the spectrum of the soluble fractions with respect to that of the corresponding BM_CS_X materials, together with a further broadening of the peak centred at 3300 cm^{-1}. These signals are ascribable to the absorption of amide and -NH moieties, thus suggesting an important presence of peptides/proteins into the soluble fraction recovered from ball-milled CS.

The film forming ability of proteins is widely reported and related to their denaturation process (Perez-Gago and Krochta, 2001; Choi and Han, 2002), which, from a molecular point of view, corresponds to an increase in disorder, free volume and mobility induced by external factors, prominently by heat. CS is detached from coffee beans during the roasting process, carried out at temperatures above 200°C (Münchow et al., 2020). Then, heat exposure during the roasting process can be considered as the main responsible for denaturation of the protein content of CS, coupled to the stress exerted by the mechano-chemical process in wet condition. This hypothesis is supported by the analysis of ^{1}H NMR spectra (Figure S6 in the Supplementary file); without entering into details, the scarce presence of resonances below 0.5

ppm and the low number of resolved peaks in the amide region (6.5 – 9.5 ppm) indicates the presence of essentially unfolded proteins (Page et al., 2005).

3.3. Coffee Silverskin Coatings: Functional Properties

CS-coated PLA films were characterized in terms of light and gas barrier, chosen as the most representative parameters for applications in the food packaging field (Mullan and McDowell, 2011).

UV-visible transmission spectra were collected on CS-coated PLA and neat PLA. All coated films show a drastic lowering of light transmittance with respect to uncoated PLA in the investigated 200–800 nm range. In particular, a transmittance reduction ranging from 97 to 99% at 400 nm of the CS coatings compared to neat PLA film was recorded, indicating high UV blocking capacity also for the thinner CS coatings (Table 2). Transmittance values, although very close one to the other, show a general decreasing trend with increasing of the coatings thickness and, for comparable thickness values, they are generally lower for CS ball-milled with higher water:CS ratio (see for example CS_BM_10:1_5.6 and CS_BM_20:1_5.8). The low transmittance of CS coatings can be ascribed to the light absorption of some of its constituents, in particular the complex aromatic structures of lignin (Li et al., 2021; Nolasco et al., 2022b), polyphenols (mainly chlorogenic acids) and other chromophores like caffeine (Bresciani et al., 2014; Machado et al., 2023). However, as CS based coatings are not perfectly transparent but translucent, an important fraction of the UV-Vis radiation is not transmitted nor absorbed but scattered by the particles and irregularities present into and onto the CS films. The slightly lower transmittance observed in CS materials treated with higher water/CS ratio can be then ascribed to the increased scattering induced by their more textured surface, as evidenced by SEM analysis (Figure 4).

Table 2. UV-Vis transmittance and transmittance reduction at 400 nm of PLA and CS_BM coatings

Sample	Transmittance (%) at 400 nm	Transmittance reduction (%) relative to PLA at 400 nm
PLA	80	-
CS_BM_10:1_2.8	2.67	96
CS_BM_10:1_5.6	0.96	99
CS_BM_13:1_2.1	1.46	98
CS_BM_13:1_4.3	1.26	98
CS_BM_20:1_1.5	1.90	97
CS_BM_20:1_2.9	1.30	98
CS_BM_20:1_5.8	0.34	99

Oxygen permeability of CS-coated PLA films was tested at 25 °C and 50% RH, in comparison to PLA. As shown in Table 3, CS coatings have a significant effect on the gas barrier properties of PLA: all coated samples show remarkable reductions of the oxygen transmission rate (OTR) of PLA, ranging from 30 % up to 91%. As expected, the coating thickness is an important factor governing the barrier properties of the samples: for each BM condition, by increasing the coatings thickness, the barrier effect increases.

Then, analyzing samples with comparable thickness but different water/CS ratio, a strong effect of water/CS ratio on the gas barrier of coatings is observed. CS_BM_20:1_Y based samples exhibit, indeed, the lowest OTR reduction values, even if samples CS_BM_20:1_2.9 and CS_BM_20:1_5.8 have very similar nominal thickness with respect to samples CS_BM_10:1_2.8 and CS_BM_10:1_5.6, respectively. The values of permeability (P O_2) of the CS coatings, calculated as detailed in the Experimental section, further underline the difference in transport behavior among CS formulations, highlighting a much higher barrier for the _10:1 and _13_1 materials with respect to the _20:1 series. Given that the differences in particle size distribution among the different compositions were limited, these results can be ascribed to a different self-assembly behavior of the coffee silverskin suspensions milled at different water/CS ratios. In general, the assembly of suspensions upon drying is guided by many factors, particularly by the evaporation kinetic of the solvent and by particle diffusion, particle-particle distance and interactions, finally leading to coalescence (Osman et al., 2017; Jiang et al., 2017). In our systems, containing many interacting components, the final structure of films is the result of a complex interplay of factors; however, we can draw some consideration on the role of water/CS ratio. High water content in the ball-milling process, and therefore in the resulting CS suspension, will produce wet coating in which CS particles are more distant from each other, and which take longer times to dry. Due to these two factors, the CS suspension may destabilize, causing CS particles to coalesce and assemble in clusters rather than form a homogenous and continuous coating. On the other hand, however, a too low amount of water will hinder the complete wetting of the particulate components of the suspension and the uniform distribution of the soluble binding phase during the deposition and drying process. In this frame, we can expect an optimal water/CS ratio to grant the best film homogeneity and, then, the higher gas barrier as reflected by the low oxygen barrier in films produced at high water/CS ratio and by the observation that both the _10:1 and _13:1 series have a much higher barrier, with the intermediate composition 13:1 performing better. It is interesting to note that the permeability values exhibited by CS films of the 10:1 and 13:1 series are comparable to that of polymeric barrier layers used in food packaging, such as Poly(ethylene naphthalate), with P O_2 at 23 °C of 0.0077 Barrer, or poly(vinyl alcohol), P O_2 in the range 0.0003 – 0.015 Barrer, dependent on humidity and crystallinity (Michiels et al., 2017).

Table 3. Oxygen transmission rate (OTR) of CS coated PLA films, OTR reduction relative to PLA, oxygen permeability (P O_2) and calculated oxygen permeability of the CS coating alone (CS P O_2) at 25 °C and 50% RH

Sample	OTR [$cm^3/(m^2$ 24h)]	OTR reduction (%)	P O_2 (Barrer)	CS P O_2 (Barrer)
PLA	438	-	0.270	-
CS_BM_10:1_2.8	89	80	0.059	0.0048
CS_BM_10:1_5.6	52	88	0.037	0.0051
CS_BM_13:1_2.1	69	84	0.045	0.0027
CS_BM_13:1_4.3	41	91	0.028	0.0030
CS_BM_20:1_1.5	308	30	0.197	0.0240
CS_BM_20:1_2.9	208	52	0.138	0.0177
CS_BM_20:1_5.8	124	72	0.088	0.0155

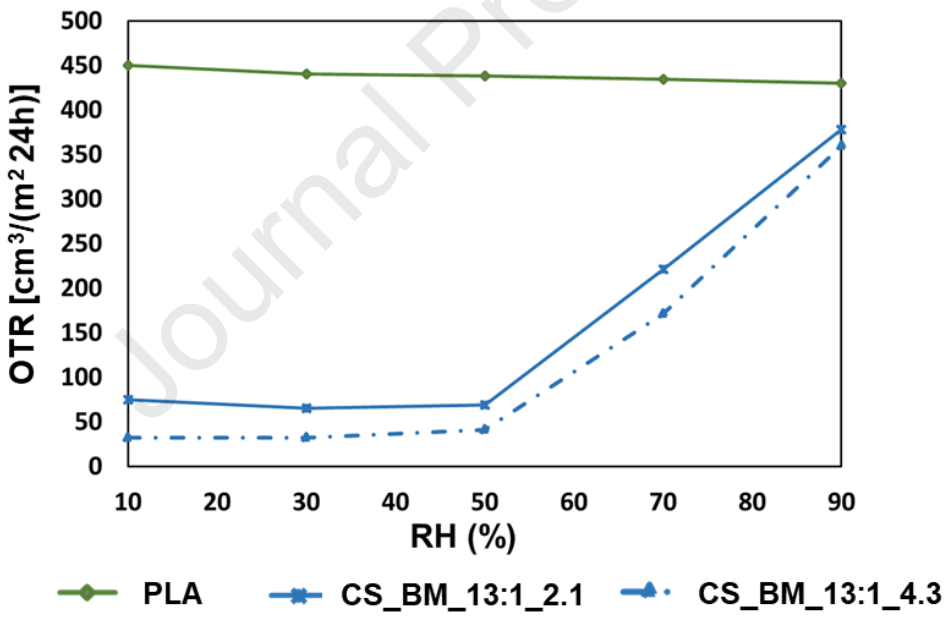

Figure 5. OTR of CS_BM_13:1_Y films and PLA at 25 °C and variable RH.

CS_BM_13:1_Y samples were tested also at variable RH conditions to investigate the dependence of OTR on the relative humidity. Results are shown in Figure 5. CS_BM_13:1_Y coatings exhibit a significant and stable O_2 barrier effect in the RH range from 10% to 50 %, with an OTR reduction of about 85-90% respect to neat PLA. Above 50% RH, the barrier properties of the coatings decreased, showing a 49-60% OTR reduction at 70% RH and 12-16% OTR reduction at 90% RH. This behaviour is a consequence of the

absorption of water by the hydrophilic CS coatings. In fact, in materials containing polar groups with high H-bond capacity water can be easily absorbed from the humid environment. And water acts in most cases as a plasticizer, increasing the free volume, therefore resulting in an increased permeation rate of gases and vapours through the material (Hong and Krochta, 2003). Thus, the plasticizing and swelling effect of moisture uptake on CS coatings results in increased permeability to O_2. This water sorption, however, did not produce a disruptive modification of the coatings, since lowering relative humidity led to a recovery of barrier properties. Indeed, further permeability measurements at 50% RH were carried out on the same areas of the CS-coated films exposed to 70% and 90% RH, showing OTR values of 86 $cm^3/(m^2$ 24h) and 73 $cm^3/(m^2$ 24h) for the 4.3 µm and the 2.1 µm coatings, respectively. These results are particularly interesting considering the reduced thickness of the tested coatings, the high hydrophilicity of CS and the very long exposure time to high RH value (about 5 hours per test).

4. Conclusions

In this work, a valorization strategy aiming at the integral recovery and recycling of coffee silverskin (CS) has been proposed. In particular, CS has been processed in a planetary ball milling in wet conditions and the effect of the mechano-chemical treatments on the morphology and properties as a function of water content was investigated. Ball milling treatments induced a drastic destructuration of CS and ball milled samples display a particle structure characterized by the primary particle size ranging from tens of nm to hundreds of nm. Then, the processed suspensions were deposited by rod coating on commercial PLA films obtaining homogeneous, well adhered and flexible coatings. The good film-forming ability has been ascribed to the presence of a protein fraction in the CS material, denaturated by both the effects of the roasting process and the mechano-chemical treatment. The coatings showed an interesting barrier to UV radiation and oxygen permeation. Finally, the oxygen permeability as a function of relative humidity was also investigated, highlighting the stability of the coating structure also upon exposure to highly humid environment. The results demonstrate the effectiveness of the proposed strategy directed at the obtainment of bio-based coatings from agricultural byproducts with potential applications in the food-packaging sector.

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Up-cycling coffee silverskin into biobased functional coatings

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Highlights

- A strategy for the integral recycling of coffee silverskin (CS) is proposed.
- Wet ball milling was used to destructure CS obtaining water suspensions.
- CS based coatings were produced onto PLA films by direct deposition of suspensions
- Good UV and oxygen barrier properties were measured on CS-coated films.

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: