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The Development of Sustainable Biocomposite Materials Based on Poly(lactic acid) and Silverskin, a Coffee Industry By-Product, for Food Packaging Applications

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Abstract: Aligned with the principles of the circular economy and aiming at the production of environmentally friendly materials for food packaging applications, sustainable biocomposite films based on poly(lactic acid) (PLA) and coffee silverskin (SS), were developed. Coffee silverskin is a by-product of the coffee roasting process, while PLA is one of the most promising bio-based polymers. Several composites were prepared with different loadings of SS, ranging from 2.5 to 20 wt.%, via the solution casting method. The findings indicated that the effective dispersion of coffee silverskin in PLA was successfully accomplished and that a bleaching treatment of the filler leads to better interfacial interaction. The addition of silverskin, in any proportion, did not affect the melting point and glass transition temperature of the polymer matrix or the oxygen permeability of the film. Moreover, the degree of swelling was increased, more so for the films with modified particles, whereas the water vapor transmission rate and permeability increased only after the addition of high amounts (>10%) of surface-treated silverskin. A gradual decrease in color lightness was measured with the increasing concentration of silverskin, and the color was more intense in the untreated samples. The antioxidant activity of the films increased gradually with increasing additions of coffee silverskin due to the presence of compounds such as polyphenols. The chemical treatment of coffee silverskin resulted in the films having improved mechanical properties, as the chemical treatment facilitated stronger bonding between the base material and the additive. Therefore, sustainable composites with enhanced antioxidant activity can be produced by the incorporation of a food industry by-product into a PLA matrix.

Keywords: PLA; coffee silverskin; composites; circular economy; antioxidant activity; gas permeability

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1. Introduction

The issue of environmental impact associated with petroleum-based plastics, which do not decompose naturally and add to pollution on land and in oceans, has led to a growing focus on the development of biodegradable packaging materials. In 2017, the global production of plastics amounted to 350 million tons, with packaging accounting for 40% of this total [1]. The primary limitation associated with biopolymeric films lies in their current higher cost relative to petroleum-based materials. A potential approach to address this issue is by developing composites that utilize polymer matrices. Opting for agricultural wastes as fillers proves to be the most efficient solution once again [2].

In the European Union, a significant quantity of food waste is produced, with an approximate annual total of 100 million tonnes, of which nearly 30% originates from the agri-food supply chain [3]. The generation of waste and by-products leads to significant environmental consequences, including land degradation, a large carbon footprint, and a substantial blue water footprint [4]. The projected rise in global food waste production to more than 200 million tons by the year 2050 underscores the critical need for effective waste management practices [5].

The growing body of research on the utilization of natural plants and agricultural waste products is aimed at addressing the dual objectives of waste reduction and the discovery of novel carbon resources. The inherent minimal toxicity displayed by plant-based substances further enhances their suitability for potential applications in areas like food packaging and biomedicine [6–10]. The coffee plant represents a significant agricultural resource for the expansion of plant-based materials, encompassing a comprehensive cycle that spans from crop cultivation and processing to the consumption of coffee beverages [5].

Considering that coffee is the second largest trade commodity, with an annual global production of 105 million tons, the coffee industry generates substantial quantities of waste throughout its processing stages from fruit to cup [11]. The annual production of coffee waste is projected to surpass 23 million tons. Its by-products mainly come from the extraction of shells and mucilaginous components from coffee fruits, and their composition varies based on the specific processing methods used, including wet or dry processing, as well as subsequent stages like roasting and brewing. Solid coffee residues include coffee pulp, coffee husks, silverskin, and spent coffee [12]. Coffee silverskin is the thin, papery skin that comes off coffee beans during roasting. While traditionally considered a waste product, coffee silverskin has gained attention for its potential applications in various industries. This by-product of the coffee industry holds significant potential as a valuable material [13] and it has attracted great interest in the formulation of biocomposites [5,14–16]. Unlike other coffee industry by-products, coffee silverskin possesses a notably low moisture content, rendering it readily usable without additional processing [17]. However, if coffee silverskin is to be utilized in polymer technology, additional grinding may be necessary, which is a common requirement for various types of materials. In terms of its composition, coffee silverskin shares similarities with other lignocellulosic materials employed in polymer technology. In addition to its fiber content, coffee silverskin generally consists of 15–19 wt% of proteins and is mainly known for its high levels of compounds with antioxidant properties [18]. Significantly, this secondary product functions as an exceptional reservoir of caffeine, polyphenols, tannins, and melanoidins, leading to a substantial level of antioxidant activity [19].

Various approaches have been proposed to address the aforementioned challenges, aiming to enhance the interaction between natural fillers and polymer matrices in order to improve the overall characteristics of biocomposites. One frequently used approach in various industries, such as the paper, textile, and polymer industries, involves the application of chemical pretreatments to the fillers. These pretreatments, such as alkali [20], bleaching, and acetylation [21], aim to enhance the properties and performance of the fillers, ultimately improving the quality of the final product [20–22]. These chemical treatments involve functional groups interacting with bio-filler structures to remove non-cellulosic elements and purify surfaces, altering compositions. This process leads to a substantial improvement in the surface roughness of the bio-fillers [22–24]. Sodium hydroxide is commonly used for alkali treatments to remove non-cellulosic components like lignins [24]. Bleaching with hydrogen peroxide can be carried out subsequently to further purify the cellulose and hemicelluloses, leading to a change in the fiber color to white. Furthermore, it enhances the surface area of the fibers, promoting better contact and interaction between the filler and matrix [20,25], thereby improving the dispersion of the bio-fillers. These treatments have been used on spent coffee grounds (SCGs), followed by the production of biocomposites through the compounding of polypropylene (PP) with these treated SCG materials, which led to their improved interfacial interaction [26].

The aim of this study was to investigate how the inclusion of coffee silverskin (ss) as an additive/reinforcement affects the characteristics of PLA-based composite films. In order to achieve this objective, various levels of particle loadings, either untreated or after surface treatments, were investigated and several biocomposites were prepared. The materials underwent additional analyses with respect to their chemical composition, morphological and thermal characteristics, oxygen and water vapor transmission rate, color, and antioxidant ability. The analytical techniques used included scanning electron

microscopy (SEM), Fourier-Transform Infra-Red (FTIR) spectroscopy, gas permeability, UV spectroscopy and Differential Scanning Calorimetry (DSC). The physico-chemical characterization of the films followed, determining their water content, film solubility, and degree of swelling. Coffee silverskin was characterized by infrared spectroscopy (FT-IR, ATR) and SEM microscopy.

2. Materials and Methods

2.1. Materials

Coffee silverskin (SS), derived from the roasting of a mixture of Arabica and Robusta coffee varieties, was provided by AVEK S.A. (Thessaloniki, Greece). Film-grade PLA Ingeo (Mw = 185,000 g/mol) was used as the materials matrix and was obtained from Nature Works LLC, Minnetonka, MN, USA, and used as received. All chemicals employed were of reagent quality.

2.2. Chemical Treatments of Coffee Silverskin

Coffee silverskin was pulverized using an electric grinder (<200 μm), washed with distilled water, and dried at 80 °C for 24 h prior to use. The chemical treatment method used was as described by Eshabir H. for spent coffee grounds, with slight modification [27]. The coffee silverskin particles underwent an alkali treatment process by immersing them in a solution of 8% aqueous sodium hydroxide (NaOH) for 24 h at room temperature, with stirring. Following this, the particles were washed extensively with distilled water (pH = 10) and then placed in a 10% acetic acid solution for a brief period, with stirring, to neutralize any remaining hydroxide (pH = 5). Subsequently, the alkali-treated particles were dried in an oven at 65 °C for 24 h. Then, the treated particles were placed in a beaker and stirred continuously in a 50 mL aqueous solution of 4% sodium hydroxide at a temperature of 90 °C for approximately 30 min using a magnetic hotplate stirrer. The bleaching treatment was then carried out by gradually adding 20 mL of hydrogen peroxide (H_2O_2) to the solution while stirring. Once the particles changed color to white, they were cooled to room temperature, separated from the solution through filtration, thoroughly washed with distilled water, and finally dried at 60 °C for 24 h (Figure 1).

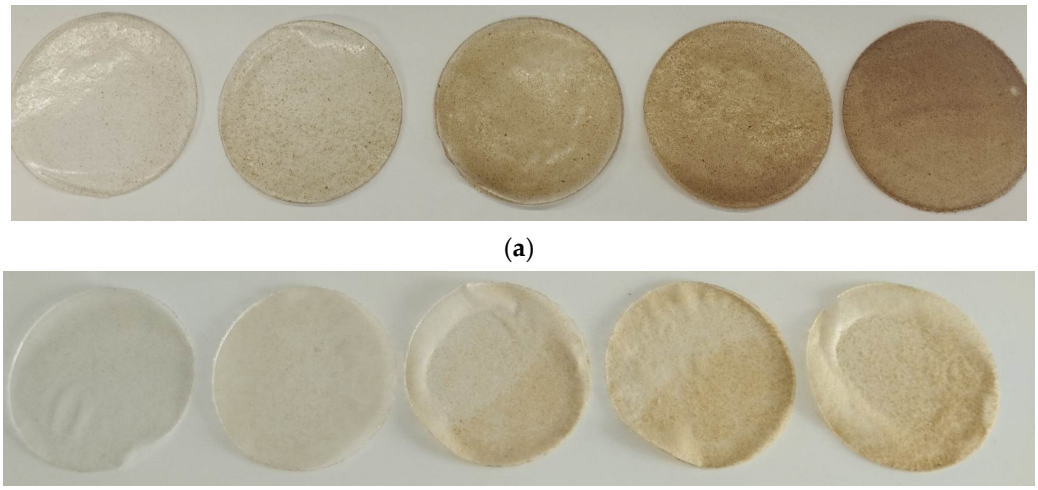


Figure 1. Untreated (brown) and treated (light brown) coffee silverskin.

2.3. Preparation of PLA Composite Films

PLA composite films were fabricated using a straightforward solution casting technique. PLA pellets were dissolved in chloroform solutions with varying concentrations of coffee silverskin (ranging from 2.5 wt.% to 20 wt.%). The mixture was heated to 60 °C for approximately 30 min, with continuous stirring on a magnetic hotplate stirrer. Subsequently, coffee silverskin, whether in its pure form or treated, was introduced into the solution, and the heating process was sustained for an additional 15 min under constant stirring. The resulting solution was then poured onto flat glass plates, allowing the solvent to evaporate naturally, and left on a flat surface at room temperature overnight. The composites prepared were given the code names PLA-2.5ss, PLA-5ss, PLA-10ss, PLA-15ss, and PLA-20ss for concentrations of untreated silverskin in the polymer matrix equal to 2.5,

5.0, 10, 15, and 20 wt% and PLA-2.5tss, PLA-5tss, PLA-10tss, PLA-15tss, and PLA-20tss for corresponding samples with treated silverskin. The composites with treated silverskin always presented a lighter color compared to those with untreated silverskin (Figure 2).



(**a**)

(**b**)

Figure 2. PLA composite films prepared with different concentrations of coffee silverskin, untreated (**a**) and treated (**b**). The darker colors correspond to increased amounts of coffee silverskin.

2.4. Material Characterization

2.4.1. Physicochemical Properties

The films' thickness was measured using a handheld micrometer with a precision of 0.01 mm. For each sample treatment, six replicates were conducted at random positions.

To determine the water content, a sample of the films, a section measuring 1 cm × 1 cm, was excised from the film and weighed before and after being placed in an oven at 105 °C for 24 h [27]. Each film underwent three replicate measurements to determine its water content using the following equation:

$$\text{Water content}(\%) = \frac{M_o - M}{M_o} \times 100 \quad (1)$$

where M_o was the initial mass (g) and M was the bone-dry mass (g).

The evaluation of the films' solubility and swelling degree was conducted by employing the methodologies described by Silva et al. [28] and Zhong et al. [29], with certain modifications [30]. Film samples underwent desiccation at 70 °C for 24 h in a vacuum oven. This procedure aimed to obtain the initial dry mass (M_1) of the films. Afterward, the desiccated films were positioned in beakers with a capacity of 50 mL, which were filled with 30 mL of distilled water. To ensure proper containment, the beakers were covered with plastic wraps and stored at a temperature of 25 °C for a period of 24 h. Following the designated period, any excess water in the beakers was disposed of, and the leftover film samples were gently dried with filter paper. These remaining film specimens (M_2) were subsequently dried once more at 70 °C for a duration of 24 h in the vacuum oven. This subsequent drying procedure was conducted to ascertain the ultimate dry weight (M_3) of the films. To ensure accuracy and consistency, three measurements were taken for each film specimen. The film solubility and swelling degree were subsequently calculated using the following respective equations:

$$\text{Film Solubility} = \frac{M_1 - M_3}{M_1} \quad (2)$$

$$\text{Swelling degree} = \frac{M_2 - M_1}{M_1} \quad (3)$$

2.4.2. Chemical Structure and Morphological Characteristics Assessed by Fourier-Transform Infra-Red (FTIR) Spectroscopy and Scanning Electron Microscopy (SEM)

For the FTIR measurements, the instrument used was the Spectrum 1 spectrophotometer from Perkin Elmer with an attenuated total reflectance (ATR) device. Measurements were carried out using thin films and spectra recorded over the range of 4000 to 650 cm^{-1} at a resolution of 2 cm^{-1}, and 32 scans were averaged to reduce noise. The instrument's software (Spectrum v5.0.1) was used to identify several peaks.

The FESEM JSM 7610 FPlus (JEOL) (JEOL, Tokyo, Japan) was employed as the scanning electron microscope in this study, with an instrument resolution of 5 nm. To ensure a proper analysis of the samples, it was necessary for them to exhibit conductivity. To achieve this, a thin carbon-layer coating was applied to the samples to enhance surface conductivity.

2.4.3. Thermal Properties Determined by Differential Scanning Calorimetry (DSC)

The DSC-Diamond (Perkin-Elmer, Akron, OH, USA) instrument was utilized to determine the glass transition temperature and melting point temperature of each prepared material. Around 5 to 6 milligrams of each sample were meticulously measured and transferred into the designated Perkin-Elmer sample container. The samples were initially heated to 200 °C at a rate of 10 °C min^{-1}. Subsequently, they were cooled to 20 °C at the same rate. The glass transition temperature and melting point temperature were measured by reheating the samples to 200 °C at a rate of 10 °C min^{-1}. It is important to note that all the results presented are obtained from the second heating process.

2.4.4. Oxygen and Water Vapor Permeability

The assessment of oxygen's permeability in the prepared films was conducted using the N500 gas permeability analyzer model manufactured by Guangzhou Biaoji Packaging Equipment Co., Ltd. (Guangzhou, China). The evaluation was carried out under specific conditions, including a constant temperature of 23 °C, relative humidity of 0%, and a gas flow rate of 10 mL/min. The ASTM E96 [31] standard was used for water vapor permeability measurements. In this experimental setup, glass Petri dishes with a diameter of 6 cm and a height of 3 cm were utilized. Each dish contained 10 mL of distilled water, resulting in a 100% humidity environment within the dish that exceeded the external humidity. Initially, films were affixed to the outer rim of the dish using paraffin, creating a gap between the films and the water level inside the dish. The dishes were subsequently positioned inside a desiccator that housed active silica gel and was weighted. The initial weight and weight over 24 h were measured. The decrease in the weight of the cup corresponds to the amount of water that has passed through the film. In order to determine the film's water vapor permeability, the initial step involved plotting the water passage curve through the film over a specific time interval and subsequently calculating the slope of the curve in its linear segment ($\Delta m/\Delta t$).

$$\text{Slope of the water passing through the film curve} = \Delta m/\Delta t \tag{4}$$

The water vapor transmission rate (*WVTR*) was evaluated using the following equation, where $\Delta m/\Delta t$ is the slope of this curve (Equation (4)) and the area of the film is A.

$$WVTR = (\Delta m/\Delta t)/A \tag{5}$$

The water vapor permeability (*WVP*) equation, Equation (6), is used where the film thickness is d_{film} and Δp is the pressure differential of the water vapor between the two sides of the film (T = 20 °C, Δp = 2339 Pa).

$$WVP = \frac{WVTR \times d_{film}}{\Delta p} = \frac{[(\Delta m/\Delta t)/A] \times d_{film}}{\Delta p} \tag{6}$$

2.4.5. Color Measurements

Measurements of the colorimetric indicators were performed using a Macbeth CE 3000 spectrophotometer (Macbeth, London, UK) under D_{65} illumination, with a 10° standard observer with ultraviolet (UV) included and a specular component included. The samples were folded twice. The reflection spectra of the samples, placed on a white calibration plate, provided their CIELAB coordinates, which include L* for luminosity, ranging from black (0) to white (100); a* for the green (−) to red (+) spectrum; and b* for the blue (−) to yellow (+) spectrum. C* (Chroma) is the color density and determines the concentration, i.e., the intensity or purity of the color or, otherwise, the relationship between the intensity and the brightness of the hue under study. Hue angle (h) is measured in degrees and specifies the hue by taking values of 0° for red–purple, 90° for yellow, 180° for cyan, and 270° for blue.

The films were tested for their color strength. The color strength (*K*/*S*) of was evaluated via a light reflectance technique using the Kubelka–Munk equation:

$$\frac{K}{S} = \frac{(1-R)^2}{2R} \tag{7}$$

where R is the reflectance at the maximum absorption wavelength, S is the scattering coefficient, and K is the absorption coefficient.

2.4.6. Antioxidant Activity

The antioxidant activity (*AA*) of the samples was assessed using the DPPH test with a Shimadzu Spectrophotometer UV-1800 (Shimadzu, Kyoto, Japan). Each film sample (6 mg) was placed in a vial with 3 mL of DPPH solution and incubated at 25 °C for 24 h in the dark. The *AA* of the films was determined by following the provided equation:

$$AA(\%) = \frac{ABS_{control} - ABS_{sample}}{ABS_{control}} \times 100 \tag{8}$$

2.4.7. Mechanical Properties

Tensile tests were performed using an Instron 3344 dynamometer, in accordance with the ASTM D882 [32], using a crosshead speed of 50 mm/min. Dumbbell-shaped tensile test specimens (central portions 5 × 0.5 mm thick, 22 mm gauge length) were cut in a Wallace cutting press. At least five measurements were conducted for each sample, and the results were averaged to obtain the mean values of their Young's modulus, tensile strength at yield, and tensile strain at break.

3. Results and Discussion

3.1. Chemical Structure and Morphological Characteristics of Coffee Silverskin and PLA/Silverskin Composites

The FTIR/ATR spectrum of coffee silverskin appears in Figure 3. A broad band appears at around 3300 cm^{-1} due to OH and NH stretching vibrations. The peak at 2920–2850 cm^{-1} is attributed to asymmetric and symmetric CH stretching, associated with the methyl group in caffeine, while the first band is reported to be related to lipids. The peak at 1640 cm^{-1} is due to carbonyl stretching (chlorogenic acid, adsorbed water), and that at 1030 cm^{-1} is due to CO stretching and CH rocking vibrations from polysaccharides such as cellulose and hemicellulose. The spectrum reveals the typical absorption bands of lignocellulosic components, which are primarily consistent in proteins, lipids, minerals, and polysaccharides (cellulose, hemicellulose) [15,16,19].

In the neat PLA spectrum (Figure 3), peaks were observed at 1740 cm^{-1} corresponding to the carbonyl (C=O) stretching band, 2960 and 2900 cm^{-1} (CH stretching), 1450 and 1365 cm^{-1} (CH bending), and 1120 and 1070 cm^{-1} (CO stretching).

Furthermore, a SEM image of coffee silverskin flakes is illustrated in Figure 4. The coffee silverskin flakes exhibited a greater presence of flaked and fibrous morphologies, which can be attributed to their origin. This coffee by-product material consists of the inner

skin of the coffee cherry [33]. The fibrous structure of coffee silverskin contributes to the formation of particles with a smoother surface and reduced porosity. Dominici et al. and Hejna et al. have both documented comparable structures in their respective works [34,35]. This can exert a substantial influence on the mechanical properties of polymer composites, as has been consistently demonstrated by numerous previous studies [36,37].

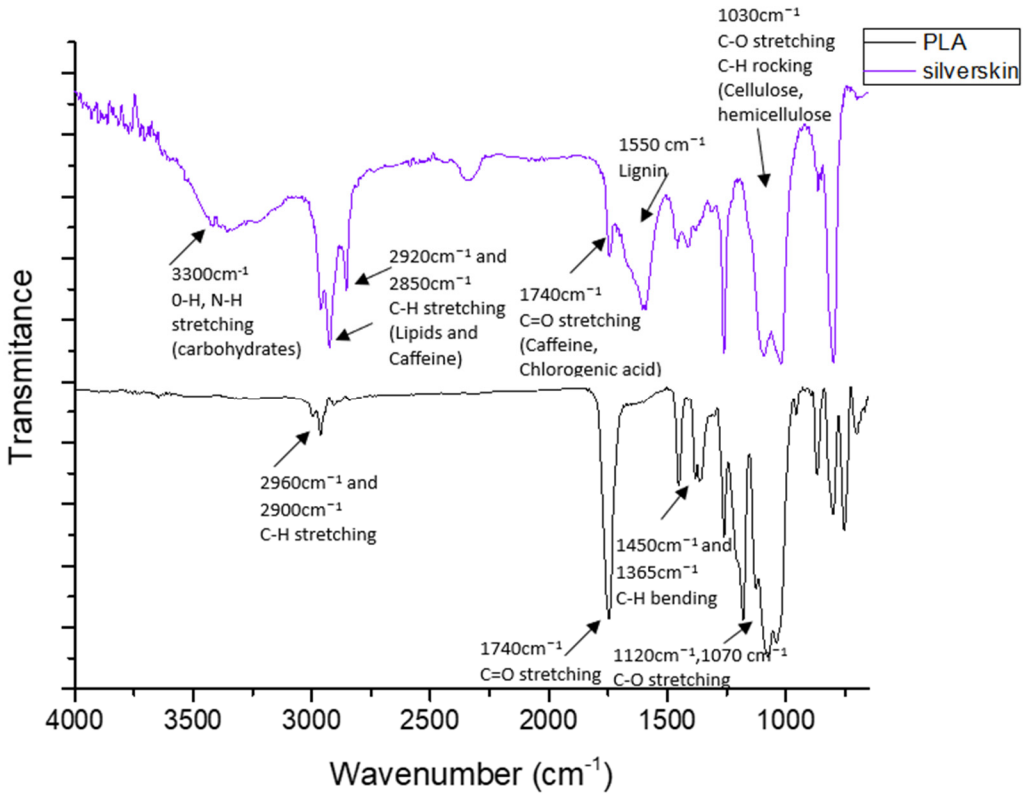


Figure 3. FTIR/ATR spectra of the coffee silverskin and PLA.

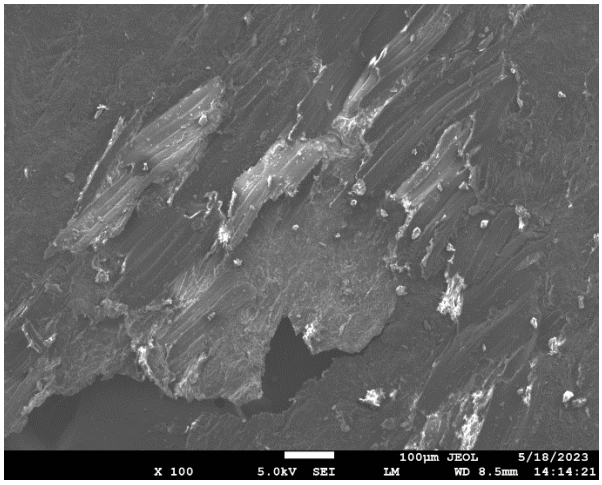


Figure 4. SEM image of coffee silverskin flakes.

Coffee silverskin contains significant quantities of proteins, as indicated in Table 1 [38]. These proteins demonstrate a consistent average density of 1.35 g/cm^3, irrespective of their composition and molecular weight [39]. Hejna et al. replaced wood flour with coffee silverskin and spent brewer's grains, which led to a decrease in the porosity of the polymer

matrix [35]. This outcome can be attributed to the elevated protein content of silverskin, which potentially functions as a plasticizer within the polymer matrix [40].

Table 1. Typical composition of coffee silverskin [39].

Component	Coffee Silverskin (Content, % Dry Mass)
Cellulose	17.9–23.8
Hemicellulose	7.5–16.9
Holocellulose	28.6–40.5
Lignin	28.6–31.0
Ash	4.5–7.6
Protein	11.8–18.7
Lipids	2.1–5.8

The morphology of untreated coffee silverskin particles was observed using scanning electron microscopy (Figure 5). The analysis revealed that these particles primarily exhibited flake-like structures, which, upon closer examination, displayed a longitudinal fibrous arrangement. This unique fibrous structure holds significant potential for silverskin's successful utilization in polymer composites [41]. As for the bleached particles, they seem to have a different morphology with an irregular spongy surface (Figure 5).

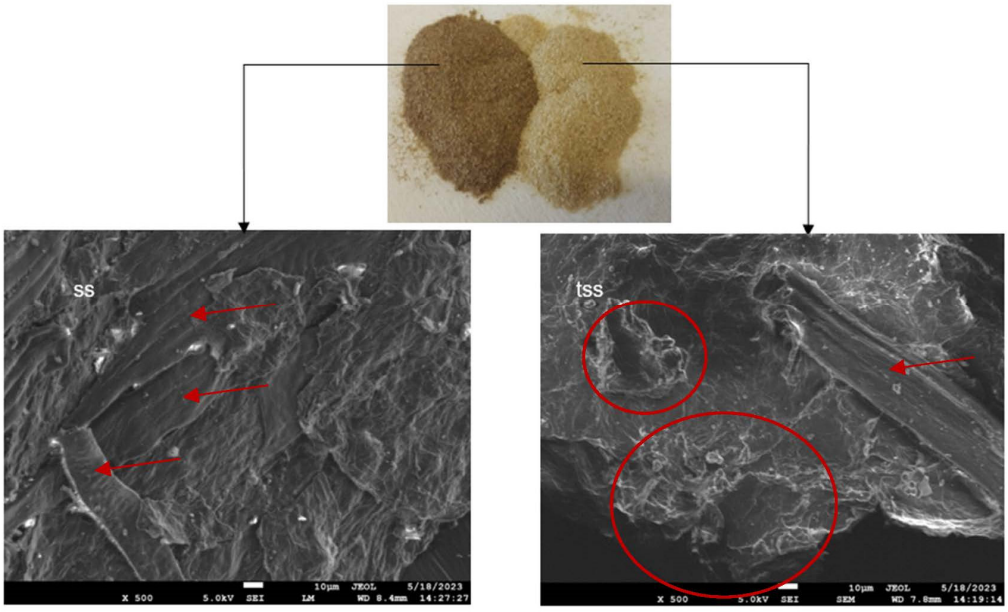


Figure 5. SEM images of the untreated (brown) and treated (light brown) coffee silverskin particles.

The structure of untreated coffee silverskin particles exhibits a lack of uniformity, as visually observed in Figure 5. The chemical treatment applied may have resulted in the elimination of non-cellulosic components and the removal of impurities that were present on the outer surface of the particles [26]. On the other hand, it is clear from Figure 5 that the bleached particles exhibit a more porous structure, with some fibrous points, compared to untreated particles and coffee silverskin flakes. In the red circles, porous structures and, with the red arrows, fibrous points are highlighted. This porous nature of the silverskin is anticipated to facilitate its favorable physical interaction with the matrix, along with an increased contact surface area.

Moreover, scanning electron microscopy was employed also to assess the surface condition, distribution, and dispersion of particles within the polymer matrix in all PLA/coffee silverskin composites. The investigation also encompassed the examination of the interfacial adhesion and morphological alterations that occurred as a consequence of the

surface treatment and processing. To assess the impact of chemical treatments on the PLA biocomposites, a comparative analysis was conducted by scrutinizing the micrographs of the PLA biocomposites alongside the untreated and treated particles. As can be seen in Figure 6, the coffee silverskin particles exhibit a random dispersion in the polymer matrix in almost all composites, with particles agglomerating when the filler is increased. The results obtained indicate that the treatments administered were effective, and the processing conditions utilized were appropriate in achieving a uniform dispersion and distribution of bleached particles. We also observed, mainly at a 20% content of coffee silverskin, that the particles that were not modified rose towards the surface of the film and seemed to disrupt it significantly. In the case of the modified particles, it seemed as if they were covered by the polymeric matrix and had a better interaction with it.

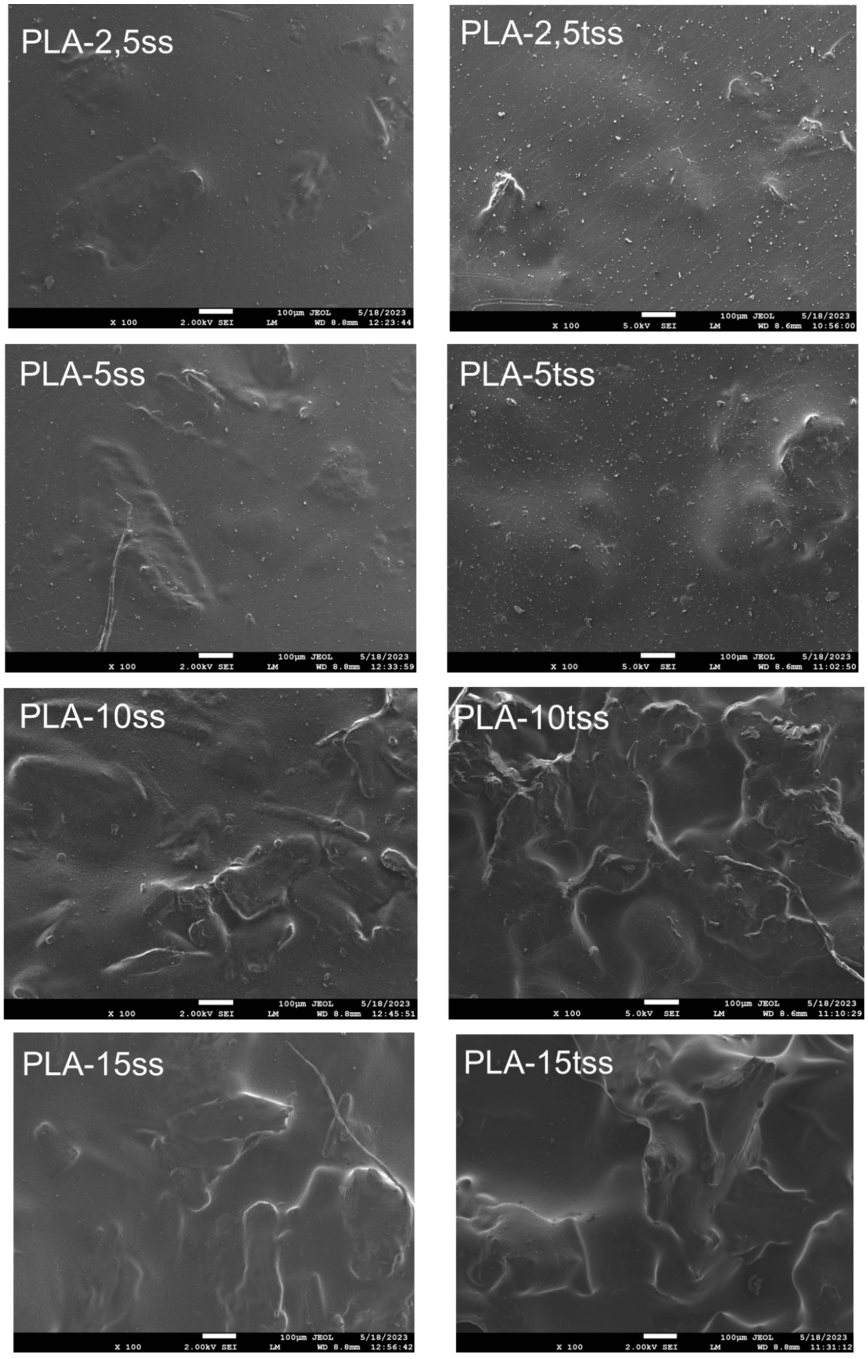


Figure 6. *Cont.*

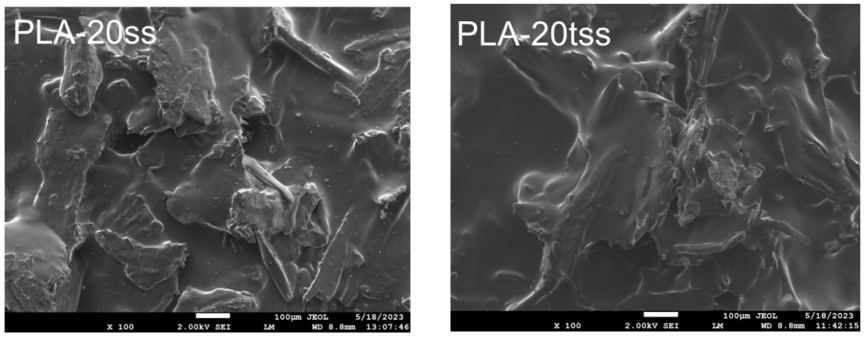


Figure 6. SEM micrographs of PLA/coffee silverskin composites containing different amounts (i.e., 2.5, 5, 10, 15, and 20 wt%) of untreated silverskin (PLA-ss) or treated silverskin (PLA-tss).

3.2. Physico-Chemical Characterization

Table 2 presents various film properties such as thickness, water content, solubility, and swelling degree, as well as Figure 7. The thickness of the film showed an increase with the addition of coffee silverskin to the film solution, both with untreated and treated particles.

Table 2. The mean and standard deviation of the physical properties of the PLA–silverskin films that were prepared.

	Thickness (μm)	Water Content (%)	Film Solubility	Swelling Degree
PLA	125 ± 10	7.83 ± 1.35	0.24 ± 0.1	1.17 ± 0.84
PLA-2.5ss	136 ± 15	8.35 ± 1.97	0.76 ± 0.1	2.29 ± 0.82
PLA-5ss	140 ± 9	8.38 ± 1.55	1.06 ± 0.16	2.39 ± 0.71
PLA-10ss	146 ± 15	8.17 ± 0.94	1.31 ± 0.3	5.26 ± 1.3
PLA-15ss	178 ± 18	5.29 ± 0.25	1.39 ± 0.4	6.35 ± 1.36
PLA-20ss	200 ± 14	7.32 ± 0.75	2.09 ± 0.7	7.29 ± 1.52
PLA-2.5tss	133 ± 12	7.96 ± 0.78	0.28 ± 0.1	1.69 ± 0.92
PLA-5tss	146 ± 12	9.67 ± 0.1	0.43 ± 0.25	2.77 ± 0.4
PLA-10tss	167 ± 13	9.48 ± 0.76	0.67 ± 0.2	7.22 ± 1.14
PLA-15tss	173 ± 15	7.09 ± 1.31	0.88 ± 0.27	9.25 ± 0.98
PLA-20tss	192 ± 19	6.90 ± 1.25	0.96 ± 0.3	10.46 ± 0.62

The water content for films with untreated particles increased compared to the control film when filler was added, up to 7.02% (PLA-5ss). With higher incorporations, the water content decreased by 24.4% (PLA-20ss) compared with the control film. As for films with bleached particles, similar behavior was observed, with an increase up to 23.5% (PLA-5tss) seen compared to the control film, which decreased by 11.8% when more coffee silverskin was added (PLA-20ss). This increase compared to the control is most likely due to the filler retaining moisture due to its hydrophilicity, while the decrease is due to aggregate formation in the filler. The composite films with untreated particles showed a better reduction of their water content. The amount of water in the HDPE composites also increased with the increase in spent coffee grounds, which are coffee by-products, such as coffee silverskin [42].

The water resistance of biodegradable films can be significantly influenced by two crucial characteristics, namely their solubility and swelling. These properties, particularly in humid conditions, play a vital role in determining the film's ability to withstand water penetration [30]. As shown in Table 2, the PLA control film exhibited low solubility and a low degree of swelling in water at 25 °C after 24 h of immersion. The incorporation of coffee silverskin into the PLA film improved neither the solubility nor the degree of swelling of the film in water. The rise in solubility can be attributed to the augmentation of the filler's composition (both untreated and treated particles), as this is a naturally occurring

substance that possesses the ability to retain moisture as a result of its inherent structure. Consequently, when the filler is submerged in water, it facilitates the absorption of a greater amount of water. The modification to the filler particles resulted in lower solubility values compared to the composites with unmodified particles. The extent of the swelling in a polymer material is greatly influenced by both the quantity and nature of its intermolecular chain interactions [43]. The incorporation of the filler led to an increase in the degree of swelling, more so for the films with modified particles of coffee silverskin. The water absorption of untreated and NaOH-treated coffee husk in a high-density polyethylene (HDPE) matrix affected its swelling too [44]. The water absorption tests demonstrated a rise in correlation with the proportion of coffee grounds present in the HDPE composites [42].

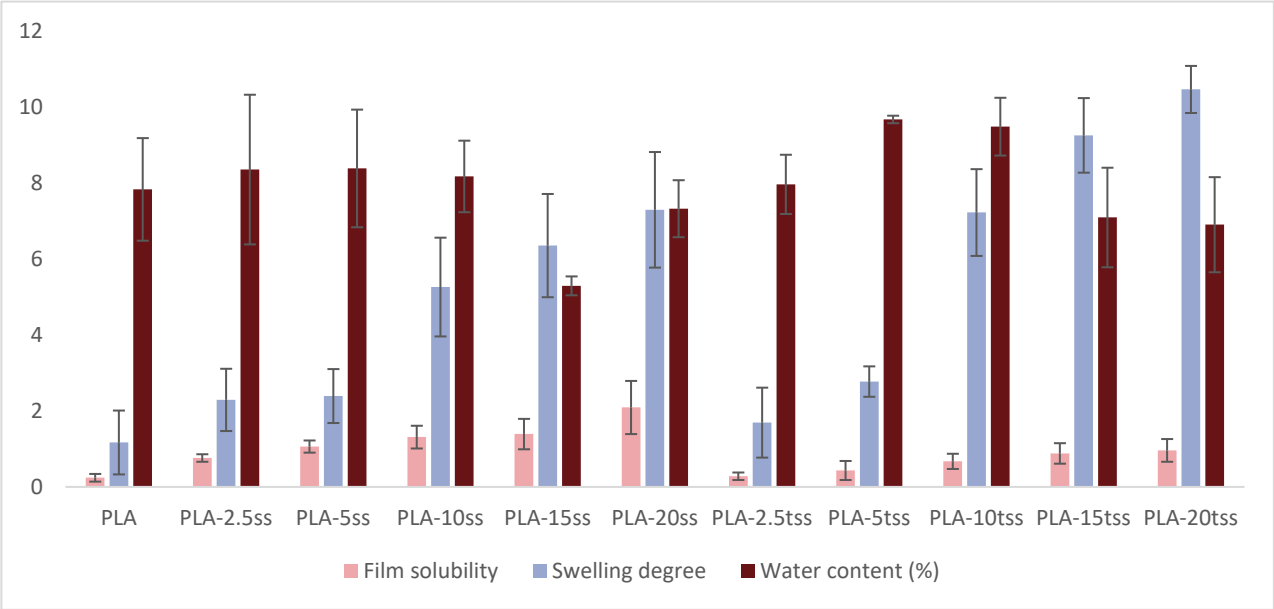


Figure 7. Physical properties of all prepared composites containing treated and untreated silverskin.

3.3. Oxygen and Water Vapor Permeability

The preservation of food quality heavily relies on the transfer of water vapor across packaging materials. As a result, there is a significant need for bio-based films that exhibit minimal water permeability. The water vapor transmission rate and permeability of all composite films are presented in Table 3. The WVTR decreased with the incorporation of untreated particles, with the largest percentage of filler being equal to the control film. The greatest reduction was observed at the lowest concentration of untreated particles. The WVTR value decreased by 15.4% compared with the control film. The addition of the modified particles to the first three concentrations did not significantly affect the WVTR, but in the last two it led to an increase of up to 48%.

Oxygen permeability was also examined, and the findings are outlined in Table 3. In terms of the oxygen permeability of the films, it is important to note that this is significantly influenced by factors such as the specific polymer grade utilized, the resulting chain's flexibility, the physical state of the polymer, and the arrangement of its molecules within the film. Consequently, comparing the data pertaining to films created from distinct polymer grades and produced under varying conditions, including the solvent employed, the type of Petri dishes utilized, and the environmental conditions (such as temperature and humidity), proves challenging [45].

Furthermore, it is a widely acknowledged fact that polymers exhibiting higher levels of crystallinity possess the ability to decrease sorption and enhance their diffusion barrier [46]. Additionally, it is well established that amorphous regions within a film are distinguished by a substantial quantity of free volume, thereby facilitating the diffusion of oxygen [45].

Table 3. Water vapor and oxygen transmission rate and water vapor permeability of all prepared composites.

	WVTR (g/m^2·d)	WVP (10^{-7}·g/(m·d·Pa)	OTR [cm^3/(m^2·d·0.1 Mpa)]
PLA	4.35	2.41	0.0013
PLA-2.5ss	3.68	2.31	0.0015
PLA-5ss	3.86	2.77	0.0014
PLA-10ss	4.07	2.45	0.0017
PLA-15ss	4.14	2.60	0.0020
PLA-20ss	4.38	3.00	0.0012
PLA-2.5tss	4.31	2.21	0.0017
PLA-5tss	4.46	2.42	0.0015
PLA-10tss	4.99	2.56	0.0015
PLA-15tss	5.52	3.00	0.0010
PLA-20tss	6.44	3.49	0.0020

The addition of modified and unmodified filler to the polymer matrix did not significantly affect the oxygen permeability of the final film at any concentration.

3.4. Color Measurement

Figure 8 and Table 4 illustrate the alteration in color of the PLA films after the incorporation of both modified and unmodified particles. Consequently, an assessment was conducted to determine the color attributes of the films. The lightness (L*) values were lower for the PLA–coffee silverskin composites compared to the control. A decrease in lightness values was observed for all the samples gradually, and these decreased by 42.66% for the max concentration of untreated particles, and by 17.66% for that of treated particles. As for the a* values, they increased gradually and higher values were observed for the films containing untreated particles, up to almost 10%. As for the films with bleached coffee silverskin, their *a** values did not increase so much, as expected. In the case of the b* values, for all the samples these were increased. A yellowish film appearance could be inferred from the combination of lower L* values and higher b* values of the films with modified coffee silverskin particles, and a brownish appearance for films with pure particles. The increased amount of SCG in the PLA matrix also led to a light brown color because of the a* and b* values' increase [47].

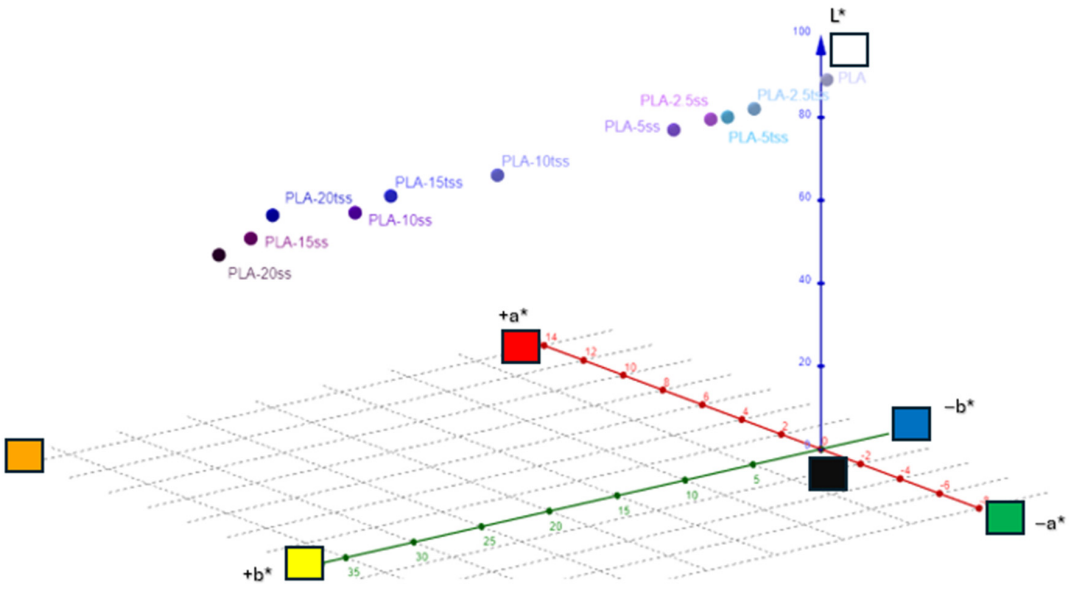


Figure 8. Color characteristics of the composite materials studied.

Table 4. Colorimetric indicators of all composite materials investigated.

	L*	a*	b*	c*	h	R% (400 nm)	K/S
PLA	91.59	−0.98	1	1.39	136.44	61.33	0.12
PLA-2.5ss	86.66	−0.36	8.64	8.6	92.41	43.03	0.38
PLA-5ss	85.21	−0.03	10.89	11.47	89.88	27.01	0.99
PLA-10ss	69.61	4.54	27.7	28.63	80.26	12.68	3.01
PLA-15ss	56.96	8.79	29.2	30.97	72.96	5.8	7.65
PLA-20ss	52.52	9.55	30.44	31.52	73.15	5.15	8.73
PLA-2.5tss	89.4	−1.27	6.77	6.81	101.33	48.76	0.27
PLA-5tss	88.77	−1.23	8.67	9.25	97.75	42.73	0.38
PLA-10tss	82.22	0.58	22.98	23.26	88.47	19.05	1.72
PLA-15tss	79.41	1.85	28.99	29.11	86.36	14.45	2.53
PLA-20tss	75.41	3.89	34.73	35.05	83.58	9.59	4.26

3.5. Thermodynamic Properties

The thermodynamic characteristics of the films fabricated using the solution casting method were analyzed through Differential Scanning Calorimetry (DSC). The glass transition temperature of the polymer could not be definitively determined from the initial heating scans (Figure 9). In all samples, a singular melting peak was observed at 146.1 °C for pure PLA and at approximately 146–149 °C for all other biocomposite materials. No instances of cold crystallization were detected, which aligns with the typical behavior of PLA films produced through solution casting [48]. Nevertheless, to eliminate the impact of the synthesis conditions and focus solely on the effect of coffee silverskin on the thermal characteristics of the poly(lactic acid), only the outcomes from subsequent heating analyses were considered. The addition of coffee silverskin led to an increase in the melting peak of PBAT, as the weight content of coffee silverskin increased by up to 20%. However, the melting temperature of PHBV remained unaffected in films containing coffee silverskin which were based on a matrix of poly(butylene adipate-co-terephthalate)/poly(3-hydroxybutyrate-co-3-hydroxyvalerate) [41].

The thermal characteristics, including the melting point (Tm) and glass transition temperature (Tg), of the films were not altered by the addition of unmodified and bleached coffee silverskin particles in any proportion to the polymer matrix (Table 5). It is evident that pure PLA demonstrated a Tg at 56.29 °C. The inclusion of different substances resulted in a reduction in Tg, with values ranging from 57 to 59 °C observed in all the composite materials. Values of T_c and T_m were also calculated for High-Density Polyethylene Composites with coffee silverskin and they were not affected when Waste Filler was added to the matrix [49]. No changes were observed in the melting and glass transition temperatures, nor was a decrease in crystallization temperature, with an increase in the amount of coffee silverskin in all the samples, with almost unaffected by the filler [2].

Table 5. Glass transition temperature, melting point, and melting enthalpy of all composites prepared, as measured by DSC.

	Tg (°C)	Tm (°C)	ΔH (J/g)
PLA	56.29	146.08	13.720
PLA-2.5ss	57.84	146.41	17.274
PLA-5ss	58.29	147.60	13.666
PLA-10ss	57.77	148.96	3.271
PLA-15ss	58.69	148.96	1.496
PLA-20ss	58.77	149.13	0.552
PLA-2.5tss	58.89	146.93	15.151
PLA-5tss	59.29	146.76	17.315
PLA-10tss	59.23	147.44	11.243
PLA-15tss	59.59	147.61	11.801
PLA-20tss	59.91	148.23	0.561

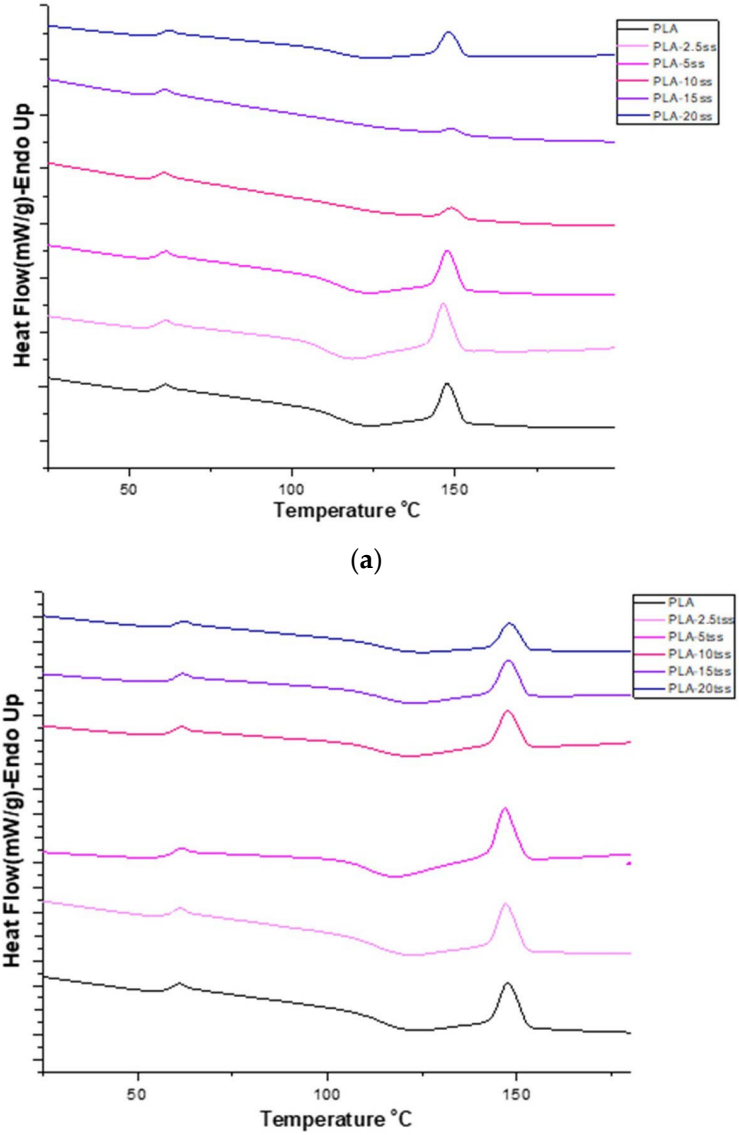


Figure 9. DSC scans of composite materials (**a**) with unmodified and (**b**) modified coffee silverskin particles. All the results presented are obtained from the second heating process.

3.6. Antioxidant Activity

The DPPH method was utilized to assess the antioxidant stability of the prepared materials. This technique is widely employed in predicting the antioxidant activity of packaging films [50]. At first, the samples displayed a purple hue, while the shift to a yellowish shade indicates the existence of antioxidant properties linked to the additive.

Antioxidant activity of the PLA-based composites containing treated and untreated silverskin at time steps of 3, 7, and 24 h is shown in Figure 10. A superior antioxidant capacity was noted in the composites with untreated particles of coffee silverskin, which increased gradually with the increasing addition of the filler into the matrix. Films with bleached silverskin particles showed an increase in antioxidant activity too, in proportion to the filler percentages, but at lower rates than the films with untreated particles (Figure 10). Thus, it is verified that coffee silverskin, as filler in a polymeric matrix, imparts antioxidant ability to a film.

Studies have shown that the antioxidant activity of coffee silverskin by DPPH has been determined to be 16.06 ± 0.08 mg TE/g_{dw} [15]. The primary source of the antioxi-

dant capacity of SS can be attributed to the presence of polyphenols. These polyphenols encompass a diverse range of compounds that possess properties for scavenging free radicals. Coffee silverskin also contains various bioactive constituents, including melanoidins, caffeine, and dietary fibers, all of which may contribute to its antioxidant activity [51]. Melanoidins, which possess substantial molecular weight, are intricate compounds that arise as a result of the Maillard reaction occurring between amino acids or proteins and sugars during the roasting of unprocessed coffee beans [52]. DPPH radical scavenging activity was calculated for films containing coffee silverskin and based on a poly(butylene adipate-co-terephthalate)/poly(3-hydroxybutyrate-co-3-hydroxyvalerate) matrix, and it showed an increase when the additive increased [41]. The HDPE–coffee silverskin composites exhibited significantly higher oxidation induction times (OITs), indicating the exceptional antioxidant properties of coffee silverskin [49].

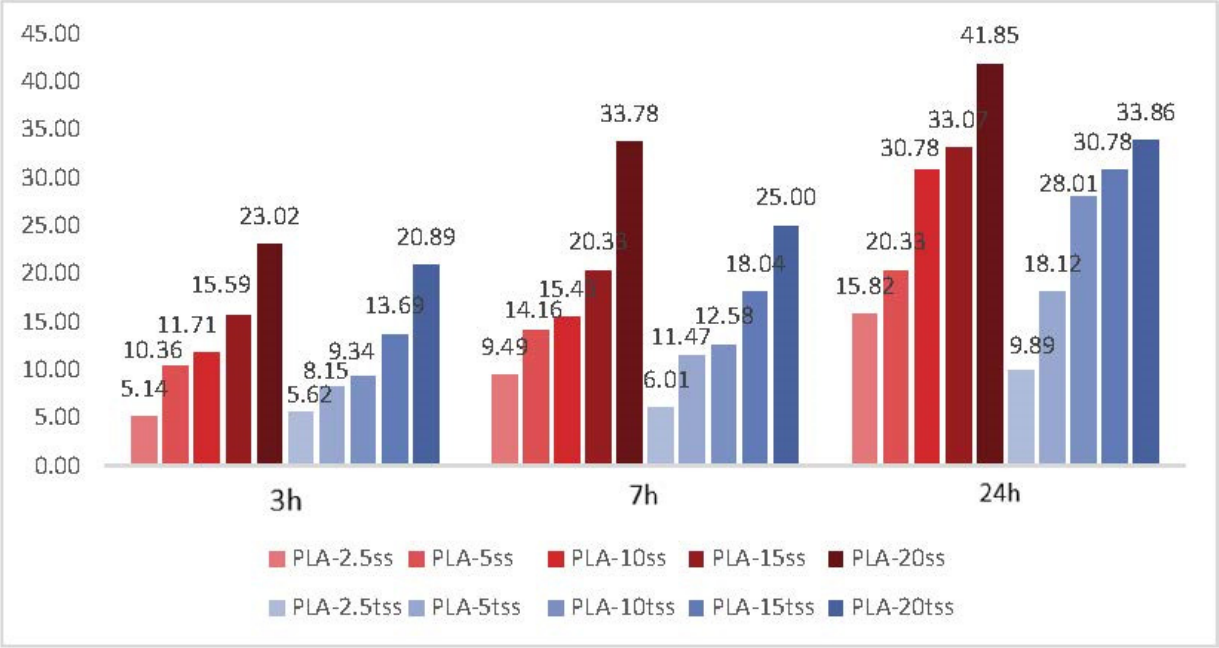


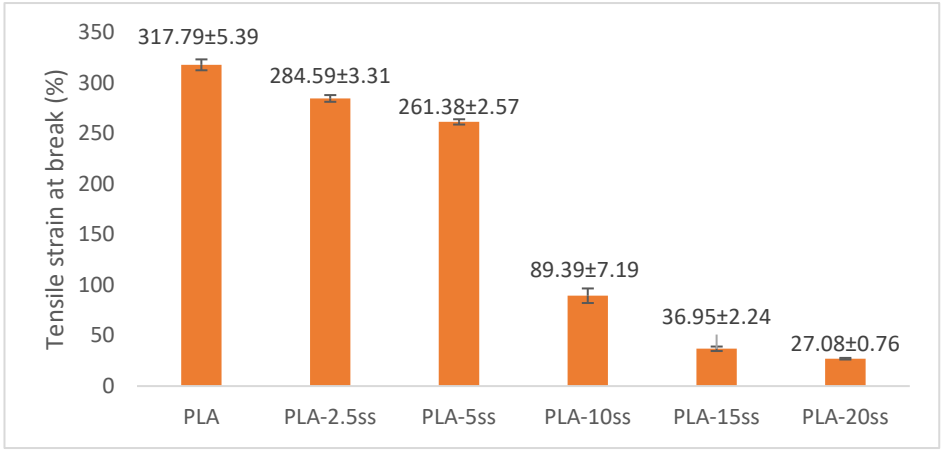
Figure 10. Antioxidant activity of the PLA-based composites containing treated and untreated silverskin at the time steps 3, 7, and 24 h.

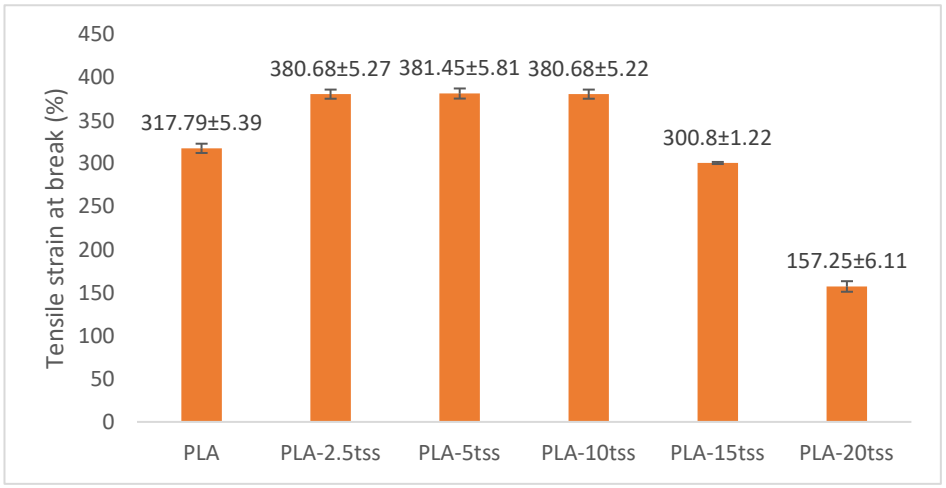
3.7. Mechanical Properties

The evaluation of a film's tensile strength and extensibility is crucial in determining its capacity to withstand the environmental stress factors commonly encountered in packaging applications. Figure 11 illustrates the films' differences in tensile strain at break (elongation %), tensile stress at yield (MPa), and E-modulus (GPa). The values were adjusted differently for the films that included unmodified and modified particles.

The tensile strain at break for the PLA-xss films decreased by up to 10.45% when coffee silverskin was added to the matrix and was 91.48% at the max concentration. Films with modified coffee silverskin had higher values of tensile strain at break, up to 20.03%, for the first three concentrations of particles in the PLA matrix. A similar value of tensile strain at break in comparison to pure PLA was observed for PLA-15tss and for PLA-20tss, with a reduction of up to 50.52%. Significantly higher values of tensile stress yield were noticed for films with modified particles of filler, up to 116.39 ± 5.36 for PLA-5tss. The rough surface of the particles, possibly caused by the chemical treatment, facilitated improved compatibility between the matrix and filler. This outcome is maybe associated with the elimination of non-cellulosic constituents from the coffee silverskin particles, resulting in enhanced interactions between the matrix and the filler. PLA-xss films exhibited lower values compared to PLA-xtss films, although they were still high. The PLA-20ss film

showed the highest value compared to the PLA-xss films, which was nearly triple that of the pure PLA film. The E-modulus of the biocomposites containing untreated coffee silverskin showed an increase with increasing amounts of additive, but it was still lower than that of the matrix. Nevertheless, composites containing treated particles exhibited higher E-modulus values compared to those with untreated ones. PLA-20tss showed significantly higher values than pure PLA, nearly doubling the observed results. Ultimately, altering the coffee silverskin resulted in the films having improved mechanical characteristics.





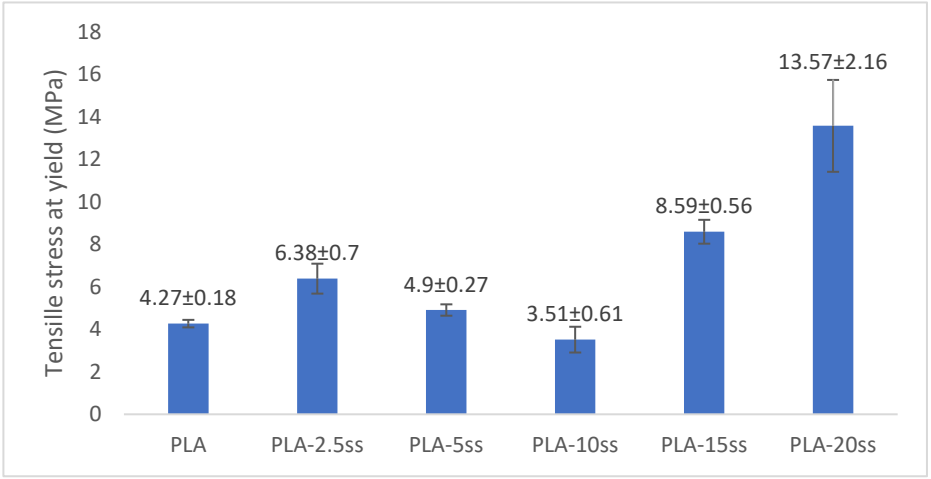


Figure 11. *Cont.*

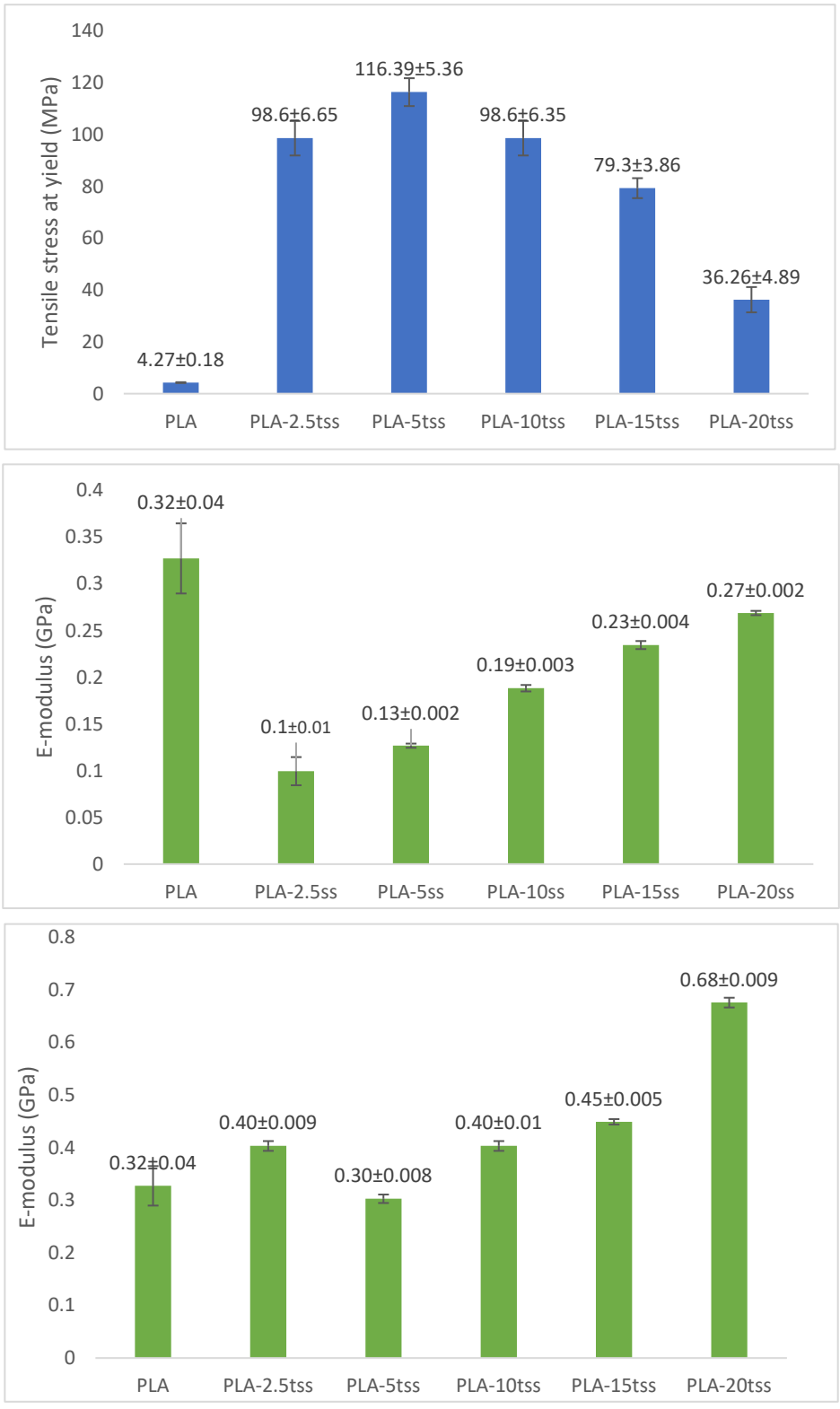


Figure 11. Mechanical properties of PLA biocomposites containing treated and untreated coffee silverskin particles.

The films of PLA and treated coffee silverskin particles produced in this work presented similar tensile stresses, lower values to their E-modulus, and a higher tensile strain at break than the cellulose matrix films made for packaging applications with chemically treated spent coffee bean powder by Sung. S. et al. (tensile stress of 105.7–149 MPa, tensile

strain of 3.5–1.1%, and E-modulus 0.855–2.18 GPa) [53]. The addition of treated spent coffee grounds, which were strengthened by the addition of bleach, to a polypropylene matrix demonstrated higher levels of E-modulus and increased its tensile strength compared to biocomposites filled with raw SCG [27]. The addition of spent coffee bean filler to poly(3-hydroxybutyrate-co-3-hydroxyvalerate) led to a reduction of tensile strength and decreased elongation values, lower than those of our films. Furthermore, it caused a reduction in the E-modulus compared to the increase we observed in our study [54]. The incorporation of coffee silverskin into PLA and PBS matrices led to lower tensile strain and stress values than in our study [16]. The inclusion of CSS progressively amplifies the value of the modulus while diminishing all other attributes, resulting in the heightened fragility of the PBSA system [2].

4. Conclusions

Various biocomposites utilizing PLA and coffee silverskin, both untreated and modified, were fabricated in the present investigation. The aim was to prepare sustainable composite materials that valorize by-products of the food industry. The materials were analyzed in relation to their chemical structure (via FTIR), morphological (by SEM) and thermal (via DSC) characteristics, oxygen and water vapor transmission rate, color, and antioxidant ability. The findings indicated a successful dispersion and distribution of silverskin in the PLA, with improved interfacial interactions due to bleaching. The addition of silverskin in any proportion did not affect the melting point and glass transition temperature of the polymer matrix. The incorporation of the filler led to an increase in the degree of swelling, and more so for the films with the modified particles of coffee silverskin. The water vapor transmission rate and permeability increased only after the addition of high amounts (>10%) of surface-treated silverskin. The oxygen permeability of the final film remained unaffected by the presence of modified or unmodified filler in the polymer matrix, regardless of the concentration. A decrease in color lightness values was observed for all samples gradually with the increasing concentration of silverskin, which was more intense in the untreated samples. Increased antioxidant activity with increased concentrations of silverskin was measured. Polyphenols are responsible for the main antioxidant activity found in coffee silverskin. Furthermore, modifying the coffee silverskin led to enhanced mechanical properties for the films, since the chemical processing promoted better adhesion between the base material and the additive.

To conclude, the integration of coffee silverskin, a coffee industry by-product, into polymer technology should be regarded as a novel approach for its economic and ecological utilization. The efficient management of this by-product has the potential to significantly reduce the manufacturing costs of polymers and polymer composites while simultaneously adding value to them. The progress made in terms of the economic aspects of coffee production is complemented by the favorable chemical composition of coffee silverskin. This by-product stands out from other lignocellulosic materials due to its abundant antioxidant compounds.

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