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XPS, SEM, DSC and Nanoindentation Characterization of Silver Nanoparticle-Coated Biopolymer Pellets

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Abstract: The development of environmentally friendly materials has been the focus of many research groups in recent years due to increased harmful effects of plastics on the environment. Bio-based materials are considered a key solution from a sustainable manufacturing perspective. The nano-coating of biopolymer blends with silver nanoparticles is the subject of challenging research projects in line with the EU Directive on environment protection and sustainable manufacturing. Coating biopolymers with silver nanoparticles provides an antimicrobial and antiviral active surface. In this work, we develop silver nanoparticle-coated biopolymer Arboblend V2 Nature pellets. The main goal is to obtain a new material with antibacterial action obtained from the blending of a biopolymer pellets with silver nanoparticles through physical vapor deposition. The study is divided in three steps. The first step represents the silver nano-coating of the Arboblend V2 Nature and the characterization of the coated/raw pellets. The second step involves the injection molding of the silver nano-coated pellets and the characterization of the samples obtained. The last step regards the press molding of the coated pellets in order to obtain thin films, as well as their characterization. The PVD-sputtering technique is used to coat the pellets with silver nanoparticles. This process is especially optimized for coating raw materials with high water content and small-size pellets. The mechanical properties, surface chemical composition and the thermal properties of the both virgin and silver nanoparticle-coated biopolymer pellets are measured and analyzed for mechanical and thermal resistance of the nano-coating layer. Differential scanning calorimetry, scanning electron microscopy, X-ray photoemission spectroscopy and nanoindentation mechanical testing is performed. The calorimetry test detects no significant alteration of the biopolymer produced from the PVD process and confirms the optimized PVD process for nano-coating of the Arboblend V2 Nature pellets with a viable application in nano-silver–biopolymer composite products.

Keywords: biopolymer; pellets; coating; silver; characterization

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1. Introduction

Developing green composites from regenerative resources has attracted the attention of many researchers worldwide as a solution for the creation of sustainable and environmentally friendly materials [1,2]. Cicala et al. [2] highlighted that the blending of different materials with renewable and easily recyclable natural resources can lead to the replacement of oil-extracted materials and wood. However, more systematic research is required to confirm the compatibility of green composite materials with the potential for blending and producing environmentally friendly materials with minimized harm to the environment. All the stages of manufacturing, synthesis, assembly and subsequent recycling of the new composite materials must be optimized and approved in order to

be used as a replacement for plastic materials. In light of this, biopolymers such as Arbofill, Arboblend and Arboform were developed for green composite applications. The authors of this article previously investigated the thermal performance and stability of Arboform LV3 Nature as a biopolymer with similar properties to plastics in terms of thermo-mechanical characteristics [3]. Depending on its type, Arboblend contains various biopolymers, lignin and other naturally derived organics such as cellulose and oils, as well as natural reinforcing fibers [4]. Beisl et al. reported that up to 100 million tons of lignin are produced each year and this is sharply increasing every year [5]. This material has a number of useful properties for high-value applications, including its chemical robustness to UV and biological environment exposure and physical stiffness [6]. Banu et al. investigated lignin-derived biopolymers for commercial applications in various fields [7,8]. As reported in [9], Arboblend V2 Nature is supplied in pellet form for usage within the polymer molding processes [10–12]. This alternative, however, competes with other composite materials, such as Arbofill Fitche and Arboform LV3 Nature. Although the properties of the Arboblend biopolymer are remarkable, there is still a need for a solution on the production and purchase costs of these granules, which are up to twice as expensive as the most common plastic, polypropylene. Arboblend has some properties that make it a viable substitute for plastic: it is manufactured from renewable raw materials and biodegradable, and if blended with other substances such as Kevlar 3%, becomes flame retardant, or when blended with silver nanoparticles, it gains an antibacterial effect against several well-known bacteria; if mixed with ceramic fibers, it gains strength, and so on. Considered as green materials, Arbofill, Arboblend and Arboform have a significant quality: these can be injected and used, melted, and reused several times with minimal changes of their properties [13]. Characterization results indicated that the performance of these biopolymers could be improved by reinforcing them with natural fibers. In a separate study, we also reported several analyses of raw materials with biodegradable capacity for additive manufacturing [14].

We reported our results on coating the pellets of the Arboblend V2 Nature biopolymer with silver nanoparticles. These results demonstrated that it is possible to blend these two unconventional materials by coating the granules of this biopolymer with silver nanoparticles using the spray-phase vapor coating process [15]. We focused on Arboblend V2 Nature pellets, because this material is biodegradable and has properties similar with plastic [13]. The PVD process was chosen because it allows the deposition of a thin layer of nanoparticles on the surface of very small pellets. Because our purpose was to obtain parts by injection molding of this mixture consisting of melting pellets that were coated with a thin layer of silver, this process ensured a better distribution of nanoparticles in the biopolymer matrix, resulting in a homogeneous mixture. Silver-coating of this biodegradable biopolymer protects the surface against bacterial contamination, especially those in public spaces [16]. Silver nanoparticles have been used for their antimicrobial action in a number of applications, including for biomedical devices [17]. The analysis on nanocomposite production to date has shown the unique physical features of these coated materials and that they can be produced with a uniform silver distribution over the polymer matrix containing anti-bacterial properties [18]. Muller et al. described several potential applications for nanocomposites and the importance of nanoblends in the automotive domain [19]. Bellisario et al. reported a detailed study on the production of silver-coated polymeric materials via the injection molding process [20]. The melting of the polymer-type material, which was previously coated with a layer of metallic nanoparticles, leads to the uniform incorporation of the nanoparticles into the polymer matrix, thus obtaining a homogeneous mixture which can subsequently be injected like any other thermoplastic material. Schneider et al. reported that a microbe's neutralization can be achieved with silver nanoparticles distributed within both natural and synthetic polymers [21].

In this work, a number of surfaces, thermal and mechanical analysis was carried out: differential scanning calorimetry (DSC), X-ray photoemission spectroscopy (XPS), scanning electron microscopy (SEM) and nanoindentation mechanical analysis. These experiments

were carried out to obtain the morphology, mechanical properties (hardness, modulus, and stress–strain analysis), surface composition analysis and thermal stability of the silver nano-coated Arboblend V2 Nature produced by the PVD process. This research aims to support the development of a new composite material with optimized antibacterial and antiviral properties.

2. Materials and Methods

Figure 1 shows the virgin and silver-coated Arboblend V2 Nature pellets, designed for injection molding, blow molding, extrusion, press molding and calendaring (density = 1.30 g·cm^3), which were supplied by Tecnaro GmbH (Germany). A 99.99% pure silver target (density = 10.49 g·cm^3) designed for the physical vapor deposition sputtering deposition process was supplied by the University of Rome "Tor Vergata" (Italy).

Figure 1. The Arboblend V2 Nature pellets: (**left**) virgin and, (**right**) silver-coated pellets.

According to the manufacturer [13], the thermoplastic material Arboblend® is based on different biopolymers such as lignin, polyester, polylactic acid, starch, bio-polyolefins, natural resins, cellulose and organic additives, but also natural reinforcing fibers. Depending on the Arboblend® type, its structure varies (up to 100% renewable raw materials) and also responds to various consumer requirements.

2.1. Fourier-Transform Infrared Spectroscopy (FT-IR)

FT-IR was performed using ATR Bruker Optics Vertex 70, with a fully attenuated reflecting cell using infrared spectra.

2.2. Pellet Preparation

A quantity of 4998 g of Arboblend V2 Nature pellets was produced. To make it possible to uniformly coat the whole quantity of pellets with silver nanoparticles, a total of five batches of pellets were sputter-coated (see Table 1).

Table 1. Parameters used for nano-silver sputter coating of the Arboblend V2 Nature.

Coating Cycles	1st	2nd	3rd	4th	5th
DS Power	300 W	330 W	423 W	430 W	430 W
Deposition time	40 min	30 min	30 min	30 min	30 min
Quantity of pellets	278 g	1388 g	1388 g	1388 g	556 g
Basket speed			23 rpm		
Gas type			Ar		
The amount of gas			100 cm^3·min		
Intensity	1.41 A	0.88 A	1.02 A	1.03 A	1.02 A

A MITEC SRL PVD sputtering system was used for the coating process. A silver target of 300 mm × 125 mm was used. The silver target used for the sputtering is shown in Figure 2.

Figure 2. The silver target used for sputtering deposition.

The stainless steel vacuum chamber had a diameter of 450 mm, a height of 600 mm, and a door for the insertion and extraction of the parts to be coated. The system was modified introducing a rotating cylindrical container with horizontal rotating axis, linked to an electric motor and mounted on the chamber door as shown in Figure 3. The vacuum was obtained with a pre-vacuum rotary vane pump (Pfeiffer Balzers Duo 030a) and a high vacuum turbomolecular pump (Pfeiffer TMH 1601). A cooler was used to chill the system door eyelet, which facilitated process visibility. An increased coating time was used for a larger number of pellets in order to obtain a similar coating thickness (see Table 1). For the first and fifth batch of Arboblend Nature V2 pellets, because the number of pellets was smaller and a longer coating time was used for batch I, it was observed that the amount of deposited silver nanoparticles was higher.

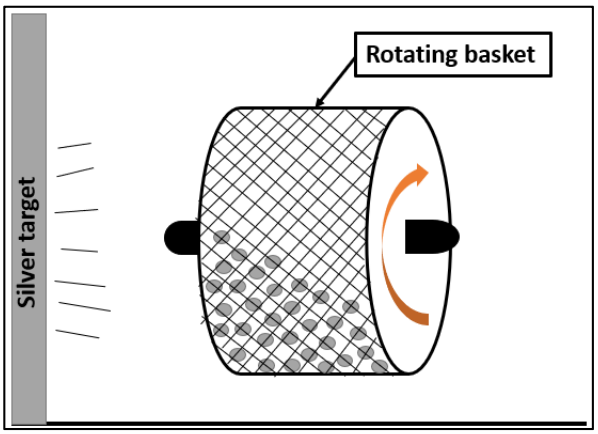


Figure 3. Schematic representation of the rotating basket, containing the Arboblend V2 Nature pellets and the silver target.

2.3. DSC Analysis

Differential scanning calorimetry measurements were recorded during heating to 100 °C for non-coated and coated samples. Sample preparation consisted of weighing both coated and raw granules, inserting them one at a time into an aluminum crucible with tweezers, and inserting them in turn into the DSC test apparatus.

2.4. Degradation of Pellets in Furnace at 500 °C

In three containers, ten uncoated Arboblend V2 Nature pellets were weighted and introduced, and in the second three, containers of coated pellets of Arboblend V2 Nature were weighted and introduced, as shown in Figure 4. Ohaus™ Pioneer™ Analytical Balances were used as the weighting apparatus, with a readability of 0.01 g.

Figure 4. The samples of Arboblend V2 Nature before being inserted in the furnace.

The containers were then placed on a metal platform in the oven at a temperature of 500 °C for 30 min. At the end of this period, the samples were returned to room temperature and re-weighed. Table 2 presents the measured data.

Table 2. Weights of the non-coated raw and coated Arboblend V2 Nature pellets.

Before					
Arboblend V2 Nature Raw Pellets			**Arboblend V2 Nature Coated Pellets**		
No	**Pellet**	**Pellet + Crucible**	**No**	**Pellet**	**Pellet + Crucible**
1	261.0 mg	12.40 g	4	260.7 mg	13.38 g
2	268.5 mg	11.56 g	5	261.5 mg	13.58 g
3	236.5 mg	11.80 g	6	256.4 mg	14.26 g
Average	255.3 mg	11.92 g	**Average**	259.5 mg	13.74 g
St. Dev.	16.73	0.43	**St. Dev.**	2.74	0.46
After					
Arboblend V2 Nature Raw Waste			**Arboblend V2 Nature Coated Waste**		
No	**Pellet**	**Pellet + Crucible**	**No**	**Pellet**	**Pellet + Crucible**
1	0.1 mg	12.14 g	4	1.7 mg	13.11 g
2	0.6 mg	11.29 g	5	0.2 mg	13.32 g
3	0.5 mg	11.54 g	6	0.4 mg	14.01 g
Average	0.4 mg	11.6 g	**Average**	0.76 mg	13.48 g
St. Dev.	0.26	0.43	**St. Dev.**	0.81	0.46

2.5. Scanning Electron Microscopy (SEM)

An EVO-LS15 Scanning Electron Microscope (SEM) was used to survey the surface microstructure morphology of the silver-coated pellets [22,23].

2.6. X-ray Photoelectron Spectroscopy (XPS Surface Analysis)

A VG Microtech X-ray photoemission spectrometer was used to measure the surface composition of the pellets with a vacuum of 10^{-9} mbar. An Mg K_{α} (h v = 1253.6 eV) X-ray source with CASAxps software was used for XPS spectrum analysis. The spectra of the binding energies were referenced to the C 1 s peak at 284.5 eV. No chemical treatments were applied on the pellets. The pellets were attached on 1 cm^2 diameter adhesive carbon pads. The literature values and the NIST X-ray Photoelectron Spectroscopy Database were used for curve fitting. For this type of analysis, the two sample types (uncoated and coated) were used. In this way, the elements that exist on the surface of the Arboblend V2 Nature uncoated and coated samples could be compared.

2.7. Nanoindentation: Mechanical Properties

Nanoindentation tests were performed on the surface of the pellets (silver coated and virgin) for hardness and modulus measurements. Images of the sample surface and indents are shown in Figure 5. A Bruker HYSITRON TI Premier was used and a force of 500 µN was applied for 5 s at several locations on the pellets. The force displacement response curves for the applied indents are shown in Figure 6.

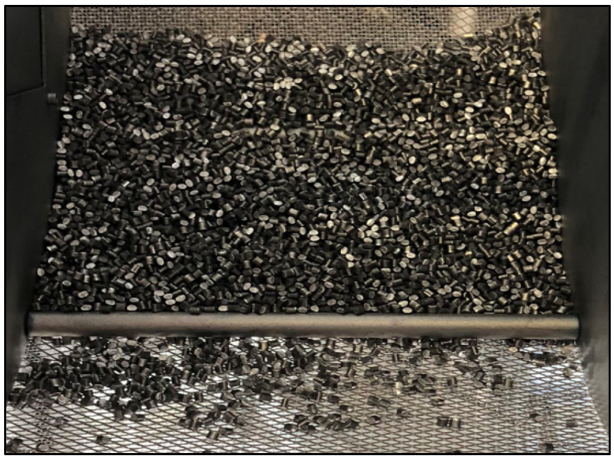


Figure 5. The first cycle of PVD coating of the Arboblend V2 Nature pellets with silver nanoparticles.

Figure 6. The results after finishing all five cycles of silver nano-coating.

3. Results

3.1. Fourier-Transform Infrared Spectroscopy (FT-IR)

The FT-IR (Fourier-transform infrared spectroscopy) analysis of our group detected lignin derivatives (2838–2950 cm^{-1}; 1715–1751 cm^{-1}), cellulose and hemicellulose (1734 cm^{-1}; 1161 cm^{-1}; 1376 cm^{-1}; 1029 cm^{-1}), amorphous and crystalline phases of polylactic acid correspondents (at 760.74 cm^{-1}) and stretching of the carbonyl group due to the presents of polylactic acid biopolymer 1738.46 cm^{-1} in the structure of this Arboblend biopolymer. The specter did not highlight the presence of polymers with aminic and/or amidic functions. Additionally, OH functions were measured with a very small concentration, which probably occurred during the manufacturing process.

3.2. Pellet Preparation

For the first coating cycle, a small number of pellets were introduced into the basket to observe if the set parameters were adapted to obtain a uniform coating for each pellet. The exposure time chosen for the first test was 40 min. As a result, the pellets obtained a uniform layer of silver nanoparticles, which means that the prolonged exposure time and the small number of pellets led to a thicker layer of silver nanoparticles, as shown in Figure 5. At fixed power, higher times were necessary for a larger number of pellets. In order to reduce the time, it was necessary to increase the power, as shown in Table 1.

For the second coating cycle, the number of pellets was up to five times higher, and trying to reduce the time to 10 min resulted in an uneven coating, with a large part of the pellets remaining uncovered because the exposure time was not long enough to cover each granule separately. As a remedy, the time was extended by 20 min, thus reaching a uniform coverage. For the third coating stage, the same period was maintained as in the second cycle: 30 min. Instead, the DC was amplified, and the power voltage and the amount of gas introduced in the vacuum chamber was diminished by 50%. The result was the expected one, obtaining a uniform coverage, much improved compared to the second cycle, and very close to the first cycle where a very small number of pellets were used.

For the fourth and fifth coating stages, the parameters and the exposure time were set as approximately the same, and the coverage was obtained as expected; Figure 6 illustrates the final result after completing all five stages of the coating.

3.3. DSC Analysis

Two wide flat peaks with a gradual sloping baseline were observed. The glass transition temperature (Tg) took place at the temperature range 50.9 °C–65 °C as shown in Figure 7. Two peaks were identified within the DSC curve, recorded during the heating of the Arboblend V2 Nature virgin material: an endothermic peak below 100 °C and an exothermal peak upon heating above 200 °C. As the heat flow between two peaks was non-linear, a solid-state endothermic reaction can be seen to have occurred during heating. A similar response was recorded for the coated material, indicating that no physical alteration of the polymer was produced from the PVD process. Regarding the peak that appeared for the temperature that was above 200°C, we consider that it could be a response at the melting point for a polymer/additive that is part of the Arboblend V2 Nature composition.

3.4. Degradation of Pellets in Furnace at 500 °C

The pellets melted at 170 °C. It can be seen that the average weight of ten silver coated pellets was, as expected, higher than that for the uncoated pellets. The overall weight loss was also greater for non-coated pellets as opposed to silver coated pellets, as per Table 3.

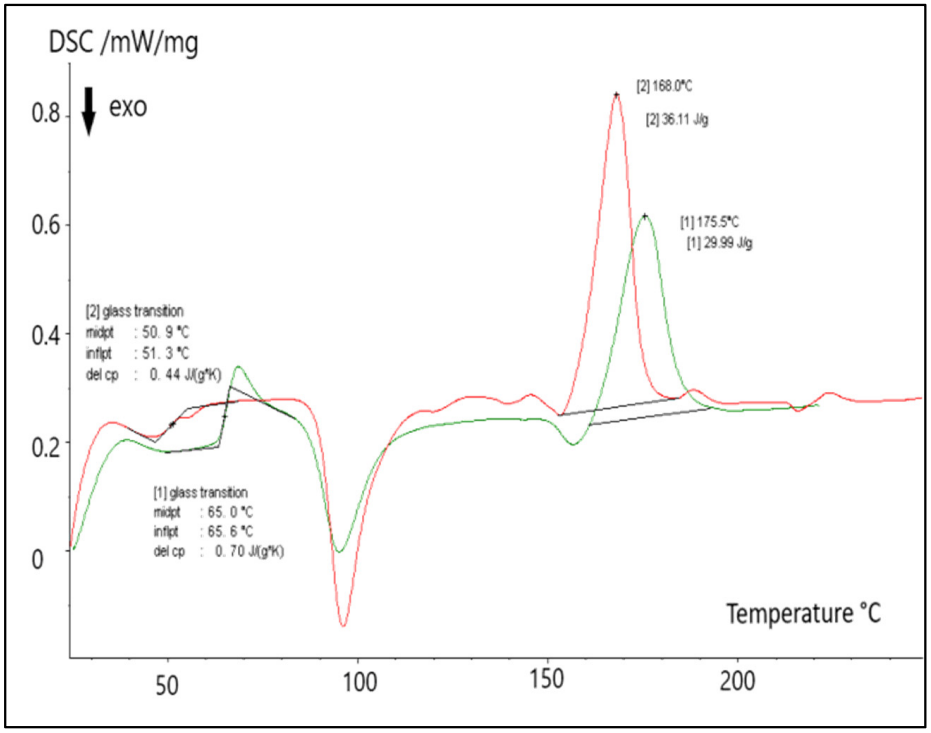
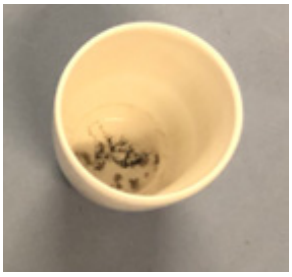


Figure 7. DSC test for silver nano-coated Arboblend V2 sample.

Table 3. Representative images for the waste left after the degradation in the furnace of the two samples.

No.	Arboblend V2 Nature Raw Waste	Arboblend V2 Nature Coated Waste
1		
2		
3		

Given the full matrix evacuation, the remaining residues were inconclusive to determine the amount of silver deposited on the coated granules because of the low value, which is comparable with differences in degradation residuals. This occurrence suggests the use of other methods, also indirect, to measure the filling contents.

3.5. Scanning Electron Microscopy (SEM)

The microstructure of the nano-coated sample displays a uniform surface structure with a random alignment of texturing (see Figure 8). In the spectrum of chemical elements recorded which were dominant on the surface, in percentage and atomic mass, carbon and oxygen were most prevalent, followed by nitrogen. The image shows a pinhole-free surface of the coating.

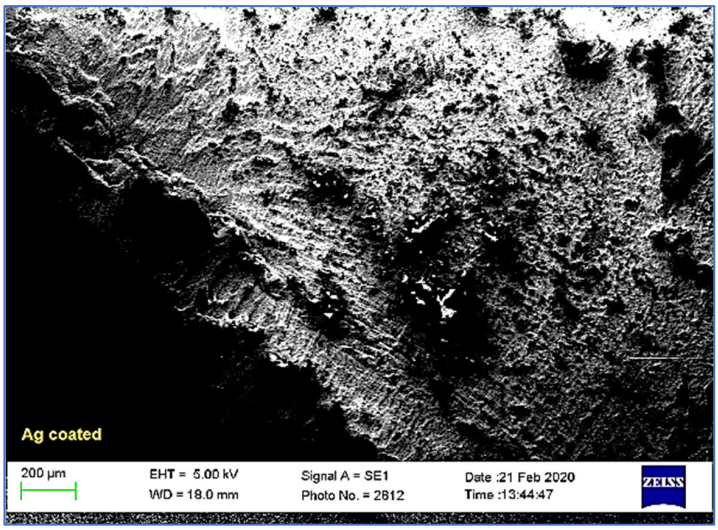


Figure 8. SEM surface morphology image of Ag-coated pellet showing a reasonably rough but well-coated surface without pinholes.

In Figure 9, we performed SEM imaging from the cross-section of the pellets. The silver coating deposited on the granule can be observed and is also labeled with the measured thickness. The thickness measurement was made in three points and the average value of the thickness is 5.53 µm. The resolution of the image is 2000×.

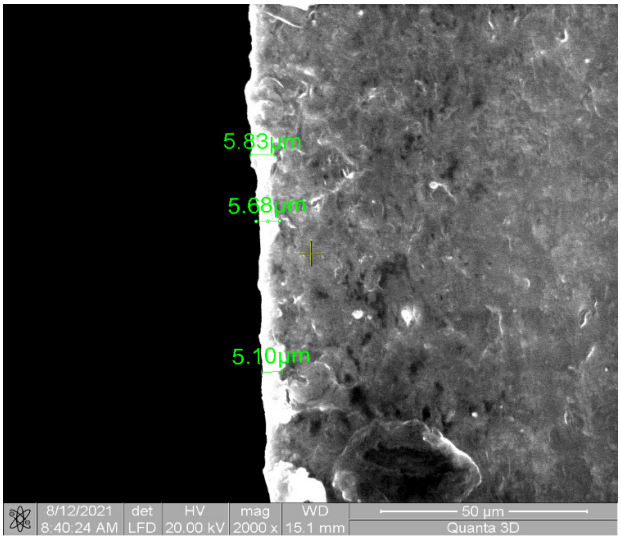


Figure 9. SEM of cross-sectioned granule of Ag-coated pellet.

3.6. X-ray Photoelectron Spectroscopy (XPS Surface Analysis)

Figure 10 shows the full surface scan of the two pellets for a wide range of binding energy from 0–700 eV. The main peaks are carbon, oxygen and silver on the Ag-coated pellet and also some Ag_2O. A different composition is noted on the surface of the Ag-coated pellet than the virgin one. The virgin sample shows more O-H and C-H compounds on the surface due to its wood nature, related to the Arboblend V2 Nature material structure. The Ag-coated samples show the associated silver peaks at the expected binding energies.

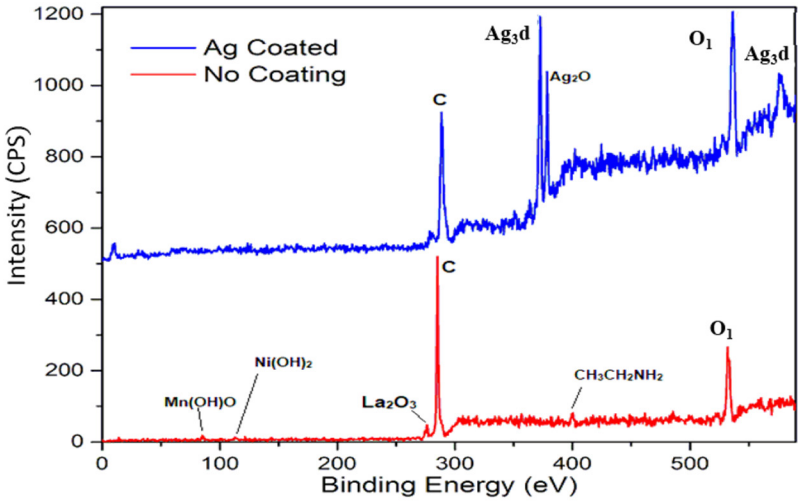


Figure 10. XPS full surface scan of the Ag-coated and virgin pellets.

A better understanding of the surface composition is obtained with XPS measurements within specific range of energies. In Figure 11, the wavelength range analysis for oxygen on the surface of the pellets is presented. The Ag-coated pellet shows a higher peak for the oxygen due to the presence of silver oxide, whereas the virgin pellet shows a smaller and broader peak. The wavelength scan range for silver detection on the pellets is shown in Figure 4 The Ag-coated pellets showed the double peak for silver as expected.

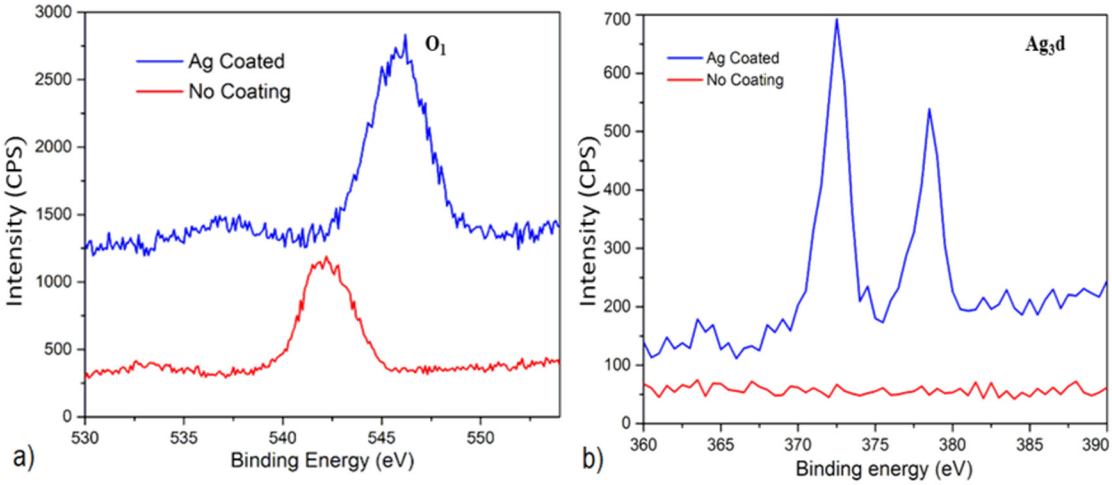


Figure 11. XPS spectrum for (**a**) oxygen and (**b**) silver, on surface of Ag-coated and virgin pellets.

3.7. Nanoindentation: Mechanical Properties

Nanoindentation tests were performed on the surface of the pellets (silver coated and virgin) for hardness and modulus measurements. Images of the sample surface and indents are shown in Figure 12. A Bruker HYSITRON TI Premier was used and a force of 500 μN

was applied for 5 s at several locations on the pellets. The force displacement response curves for the applied indents are shown in Figure 13. The Ag-coated pellets showed a more defined sharper indent under an optical scan of the indent due to the coverage by the nano-silver layer. For this experiment, the pellets were mounted on the carbon pads to keep them tight under the indent force. The indentation was repeated several times to determine the average hardness and modulus values.

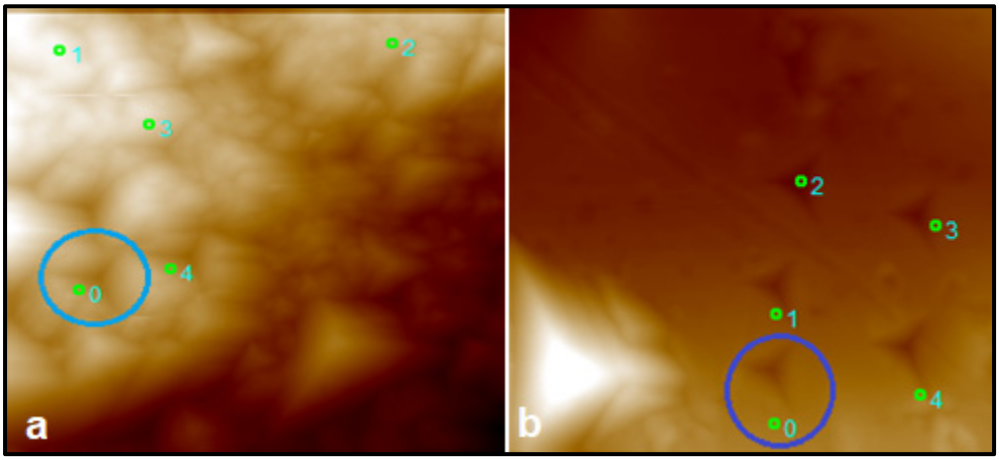


Figure 12. Micrograph of the nano-indentation on the surface of (**a**) virgin and (**b**) Ag-coated pellets.

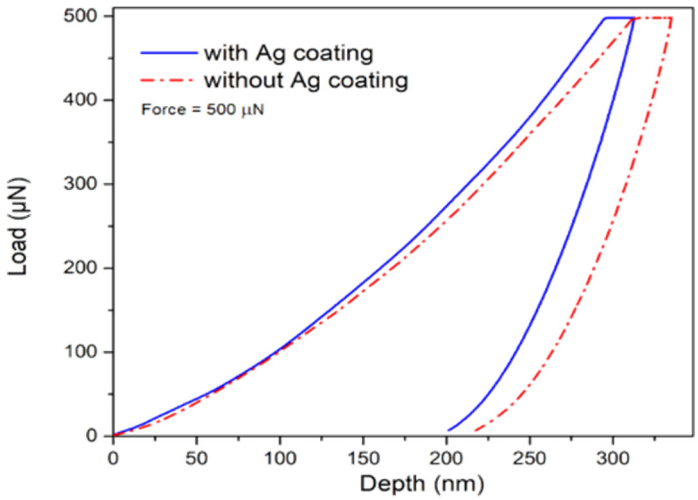


Figure 13. Force vs. displacement depth profiles for the virgin and Ag-coated pellets under force of 500 μN for 5 seconds.

Figure 14 shows the hardness and effective modules of the virgin and Ag-coated pellets. A smaller effective module (4.95 GPa) for the Ag-coated sample was obtained. This was due to the indent main impinging on the nanoparticle coating of the pellet. The hardness and modulus of the virgin pellet were higher as these indents were directly into the pellet surface. The average values are noted in Table 4. The hardness and effective modulus is lower for the silver-coated pellets, which might be due to the higher surface roughness of the Ag-coated pellets or due to the changed morphology of the coated films, which has to be optimized to improve the morphology of the coating film.

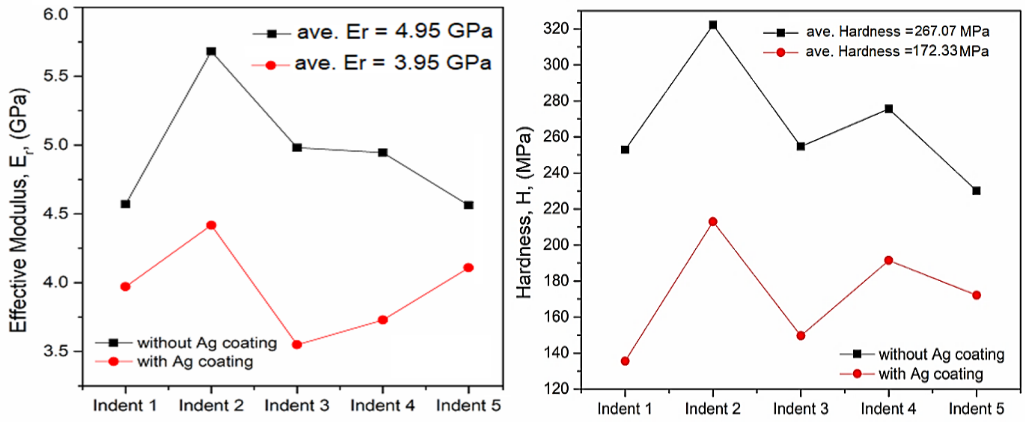


Figure 14. The effective modules and hardness extracted from indentation measurements.

Table 4. The individual and average hardness and modulus values for the uncoated and coated Arboblend V2 Nature pellets extracted from nano-indentation measurements.

Nanoindentation on Raw and Ag-Coated Pellets for Arboblend V2 Nature					
HARDNESS (MPa)			EFFECTIVE MODULUS (GPa)		
No	**Raw Pellets**	**Ag-Coated Pellets**	**No**	**Raw Pellets**	**Ag-Coated Pellets**
Indent 1	252.81	135.54	Indent 1	4.57	3.97
Indent 2	322.18	212.97	Indent 2	5.68	4.41
Indent 3	254.62	149.56	Indent 3	4.98	3.54
Indent 4	275.56	191.47	Indent 4	4.94	3.72
Indent 5	230.19	172.11	Indent 5	4.56	4.10
Average	267.07	172.33	**Average**	4.94	3.95
St. Dev	34.74	31.18	**St. Dev**	0.45	0.33

4. Conclusions

The purpose of this study was to examine the thermo-mechanical and surface composition properties of biopolymer materials, which could be applied for their environmentally friendly and antimicrobial applications. Biopolymer-based Arboblend V2 Nature pellets were silver nanoparticles coated with the physical vapor deposition sputtering deposition process. Both non-coated and silver-coated pellets were examined by mechanical, thermal and surface composition and morphology analysis. Nano-coating fragmentation allows silver nano-particles to be distributed onto the polymer surface in very low concentrations. A uniform dispersion of nanoparticles in the polymer matrix can lead to a significant improvement in the properties of the nanocomposites. This research project consists of two main phases: the first step was to coat the Arboblend V2 Nature pellets and characterize these pellets relative to the virgin pellets, and the second phase of characterizing parts produced with these materials via injection molding is still in progress. DSC analysis, degradation in the oven test, scanning electron microscopy, X-ray diffraction analysis, and nanoindentation characterization of the samples was performed. DSC analysis revealed that no chemical alteration of the polymer resulted from the PVD process. The SEM analysis for the virgin liquid wood displayed a uniform surface pinhole-free coated surface structure with a random microstructure alignment. X-ray photoemission spectroscopy revealed that the main peaks were carbon, oxygen, and on the silver coated samples, also silver and Ag_2O. The virgin sample showed more O-H and C-H compounds on the surface due to its wood nature related to the Arboblend V2 Nature material structure. Nanoindentation tests on the surface of the pellets for silver-coated pellets showed a sharper indent under the optical scan of the indent due to the silver surface layer coverage. In future work, parts with these starting feedstocks will be obtained by injection molding and tested to accurately determine the macroscopic properties of the new material.

Author Contributions: J.G.M.: Writing—original draft, methodology, experimental research; N.E.G.: XPS, SEM, nanoindentation experiments, data analysis, writing the manuscript; D.N.: writing—original draft, writing—review and editing; D.B.: experimental research—review and editing; F.Q.: experimental research, coating and PVS. All authors have read and agreed to the published version of the manuscript.

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Informed Consent Statement: Not applicable.

Data Availability Statement: The datasets generated during and/or analyzed during the current study are available from the corresponding author on reasonable request.

Conflicts of Interest: No conflict of interest.

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