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OTR and surface-wetting of coated Arboblend V2 Nature sheets

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Abstract. The manuscript presents the barrier properties of Arboblend V2 Nature and Arboblend V2 Nature reinforced by coating granules with silver nanoparticles, regarding the contact angle and oxygen transmission rate. Also, are highlighted compression molding stages used in order to obtain the test samples - thin sheets. Following the obtained results is observed that by using the PVD coating the oxygen transmission ratio is reduced up to 32% compared to the base material. This improvement is due to the small silver nanoparticles that were uniformly deposited on the surface of Arboblend V2 Nature granules. In what concern the surface-wetting of the analysed samples, a small but obvious improvement takes place, the difference between the average contact angles being approximatively 5°.

Keywords: OTR, surface-wetting, coating, silver nanoparticles, biopolymer.

1. Introduction

Due to the fact that synthetic polymeric materials have been and still are for a good period of time used in food packaging industry, their effect become a serious ecological problem. Thus, the substitution with friendly packaging materials has become mandatory, but the change cannot be done immediately nevertheless gradually due to their spread. Also, it is necessary to find viable alternatives. Biodegradable polymeric materials are the main alternative but the research is

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continuously progress. A simple and widely used method to investigate the surface characteristics of solid materials is the contact angle measurement for varied applications as ink-jet and spray cooling technologies or special-wetting surfaces [1]. The concept of contact angle, θ, it's older than 200 years, and is a macroscopic presentation of the complex interaction between a solid surface and a liquid drop. The measurement can provide information regarding the surface topography, chemistry, and capillary forces at nano- or micro- scale, [2, 3].
The OTR sheets are affected by factors as: thickness of barrier layer (barrier is increasing with the layer thickness); base film surface compatibility; polymerization process, plasticizer content and copolymer ratio, [4 - 6].
It is essential and normal that with the evolution of technology and food packaging (even some non-food packaging for products where atmospheric oxygen is harmful) progress through researchers who develop ways / materials that reduce oxygen exposure and extend the shelf life of oxygen-sensitive foods.
In the idea of supporting the current recycling / biodegradation trend, the present paper aims to investigate the behavior of the compresed samples from Arboblend V2 Nature lignin-based polymer after coating with silver nanoparticles (AgNP's). The coated layer has very small dimensions, in the order of micrometers, [7], in order to affect as small as possible the biodegradation rate of the substrate - Arboblend V2 Nature (thermoplastic from renewable resources, [8, 9]).

2. Materials and methods

The samples processed during the experimental researches were obtained from Arboblend V2 Nature granules coated with silver nanoparticles (AgNP's). Coating was realized by using PVD (Physical Vapor Deposition) process at University of Rome, "Tor Vergata", Industrial Engineering Department, Italy. Also, the compression molding of the silver nano-coated granules was completed at the same university.
In order to observe more precise, the advantages of this type of coating two types of samples (disks sheet) were obtained, a image of them being surprised in Figure 1.

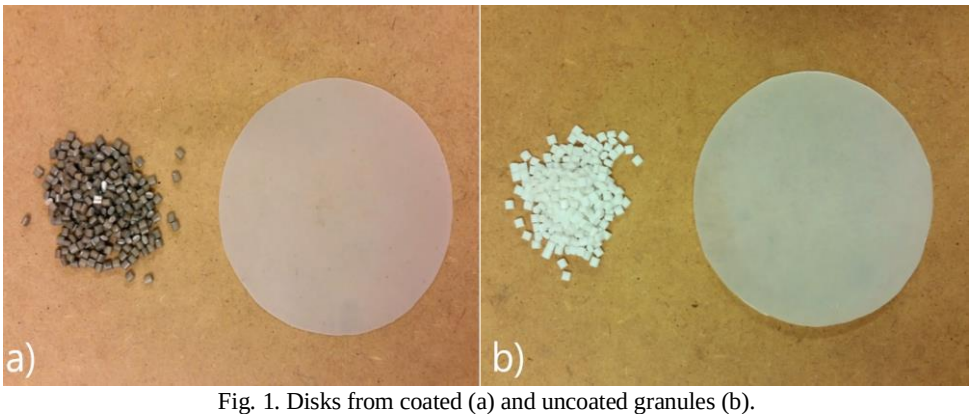


Fig. 1. Disks from coated (a) and uncoated granules (b).

Compression molding of Arboblend V2 Nature granules + AgNP's was realised under the hydraulic piston and did not use a compression moulding machine, being a laboratory practice.
In the first tests, disks (sheets) were compression moulded from coated granules without any additional step. As a result, poor mixing is observed, with the maximum presence of silver nanoparticles in the centre of the moulded disk. Subsequently, compression moulding was performed after melting and mixing of the coated granules in an aluminium crucible. After mixing, the blend was placed on a plate and heated together with a punch for successive compression moulding under the hydraulic press (Figure 2).

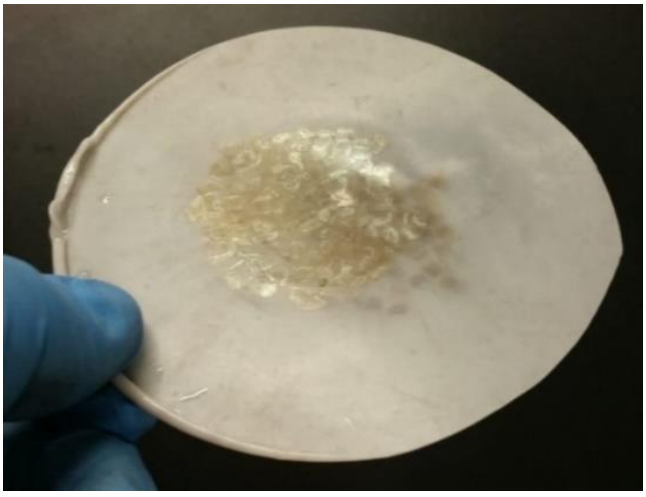


Fig. 2. Compression molding of coated granules.

Thanks to this laboratory procedure the final silver dispersion is strongly improved even if some defects are still possible (such as bubbles from polymer degradation or dendritic structures). A further improvement consisted in cooling the mold with water at the end of moulding thus reducing the amount of heat provided to the disk sheet. In Table 1 are presented the main parameters selected / measured in order to obtain the samples:

Table 1. Compression moulding parameters

Parameter	*Value*
Weight of pellets	2.2 g
Initial mold temperature	225°C
Molding time	5 min

In the final process, disks were flexible, with low defects and enough homogeneous in thickness, Figure 3. In particular, it was observed that flexibility was easier to be obtained with coated pellets while the virgin pellets lead to brittle disks, probably due to higher crystallinity. The disks are about 80 mm in diameter.

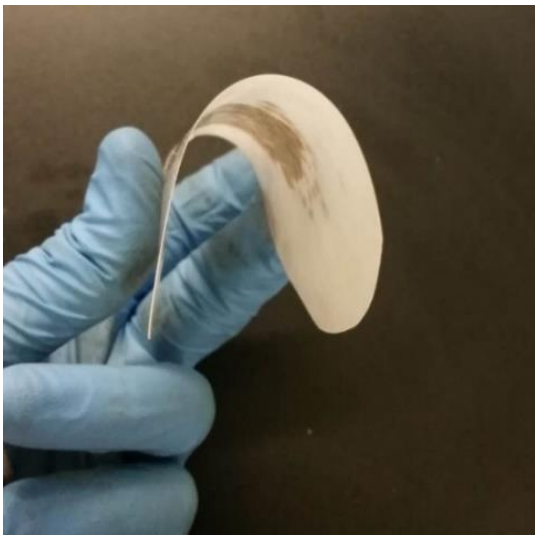


Fig. 3. Flexible Disk sheet.

Permeability tests were made on one sample for coated and uncoated samples, Figure 1 (a - b). The test conditions for the two types of samples are visible in Table 2.

Table 2. OTR measurement parameters

Parameter \ Sample	Sheet obtained from raw Arboblend V2 Nature granules	Sheet obtained from silver nano-coated Arboblend V2 Nature granules
Surface	50 [cm²]	50 [cm²]
Average thickness	187 [µm]	245 [µm]
Test temperature	23.00 [°C]	23.00[°C]
Relative moisture	50.00 [%]	50.00 [%]
Conditioning time	19 [h]	25 [h]
Measuring time	2[h] 13[min]	3[h] 2[min]

An Attention® Theta optical tensiometer (T200) was selected to evaluate the *contact angle measurements* using distilled water. The tests were executed at room temperature (20°C) and for each sample an average of 10 measurements at different locations were collected. Drops of 3 µl were automatically dispensed on the different surfaces of the two samples: raw Arboblend V2 Nature (Figure 4(a)) and Arboblend V2 Nature with silver nanoparticles (Figure 4(b)). The contact time of the drop on the surface has been fixed to 30s.

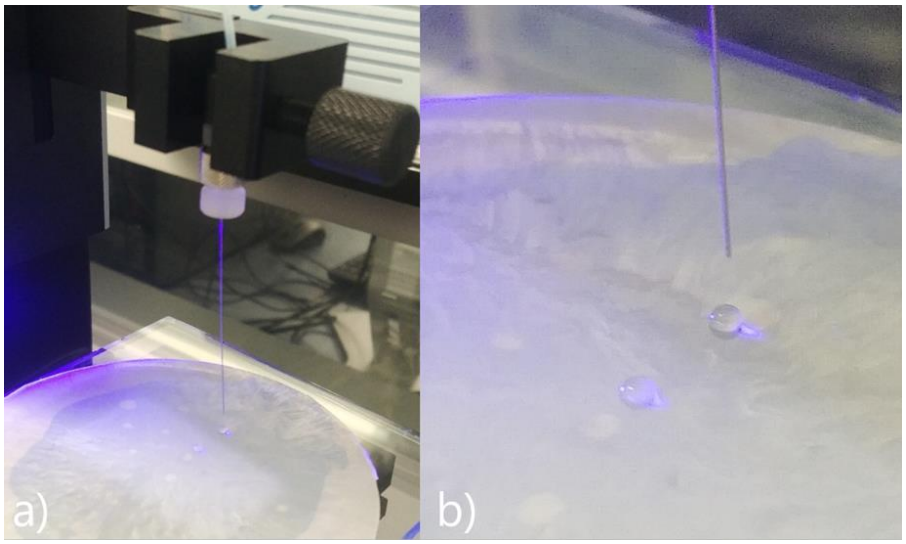


Fig. 4. Dispersing water drops on: (a) Arboblend V2 Nature disk;
(b) Arboblend V2 Nature with AgNP's.

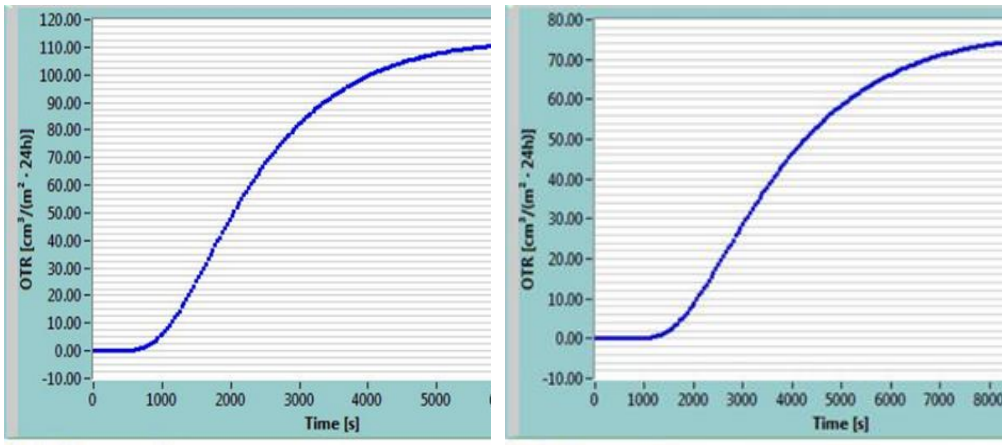
3. Results and discussions

3.1. Oxygen Permeability Test

In what concern the obtained results these ones are highlighted in Table 3 and Figure 5. Being different in thickness, the barrier efficiency may be measured by the reverse of the product between the OTR and the average thickness. An increment over 12.48% of the passive barrier to oxygen has been measured thanks to the presence of silver nanoparticles. And, the oxygen transmission rate values have decreased with 32% by coating of Arboblend V2 Nature granules.

Table 3. Results of the Oxygen Permeability Test

Result \ Sample	Sheet obtained from raw Arboblend V2 Nature granules	Sheet obtained from silver nano-coated Arboblend V2 Nature granules
Oxygen Transmission Rate (OTR)	110.77 [$cm^3/ (m^2 \cdot 24h)$]	75.16 [$cm^3/ (m^2 \cdot 24h)$]
Barrier efficiency	**4.827** (10^5/OTR*t)	**5.43** (10^5/OTR*t)



Arboblend V2 Nature sheet Arboblend V2 Nature + AgNP's sheet

Fig. 5. Oxygen Transmission Rate graphs.

3.2. Contact angle measurement

The right, left and mean CA (contact angle) were evaluated for each measure. In particular, mean CA values at 10 s from the drop deposition were analyzed (Table 4). The results showed a small increase in the CA for the material with AgNP's (Figure 6).

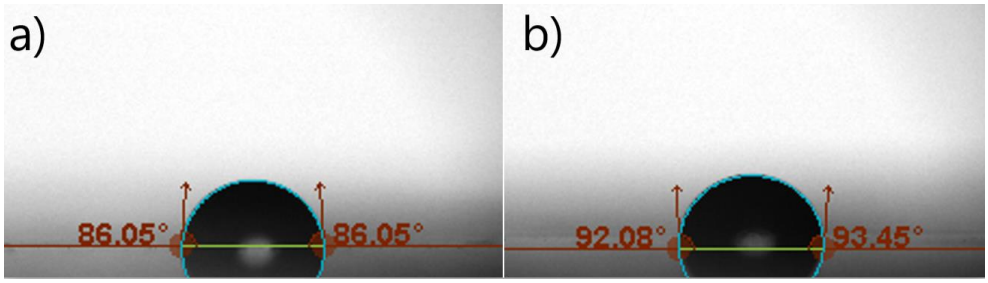


Fig. 6. Contact angle results: a) for Arboblend V2 Nature sheet, b) for Arboblend V2 Nature with AgNP's sheet.

In case of Arboblend V2 Nature material the mean value of CA is 87.73±2.88) and based on this it can be conclude that the lignin-based polymer reflects a hydrophilic character at the upper limit. Moreover, due to the fact that the CA value is very close to 90˚ an incomplete wetting of the surface took please. In terms of sheet made of Arboblend V2 Nature + AgNP's, the value above the 90° limit, more precisely an average value of 92.99±3.78, indicates the hydrophobic character of this one.

Table 4. CA mean values at 10s from drop deposition (CAa: average value, Δ: standard deviation)

	CA mean value[°]											
Test no.	1	2	3	4	5	6	7	8	9	10	**CAa [°]**	**Δ [°]**
Arboblend V2 Nature + AgNP's	97.05	91.71	86.62	92.22	96.02	89.04	90.33	92.77	95.78	98.45	**92.99**	**3.78**
Arboblend V2 Nature	90	94.03	86.05	86.05	90.04	86.16	85.15	88.07	87.09	84.66	**87.73**	**2.88**

Figure 7 highlights the distribution of CA measurements for the two analyzed materials. It is observed that only two of the wetting tests recorded values below 90° most likely due to structural inhomogeneities related to the distribution of AgNP's in the polymeric mass.

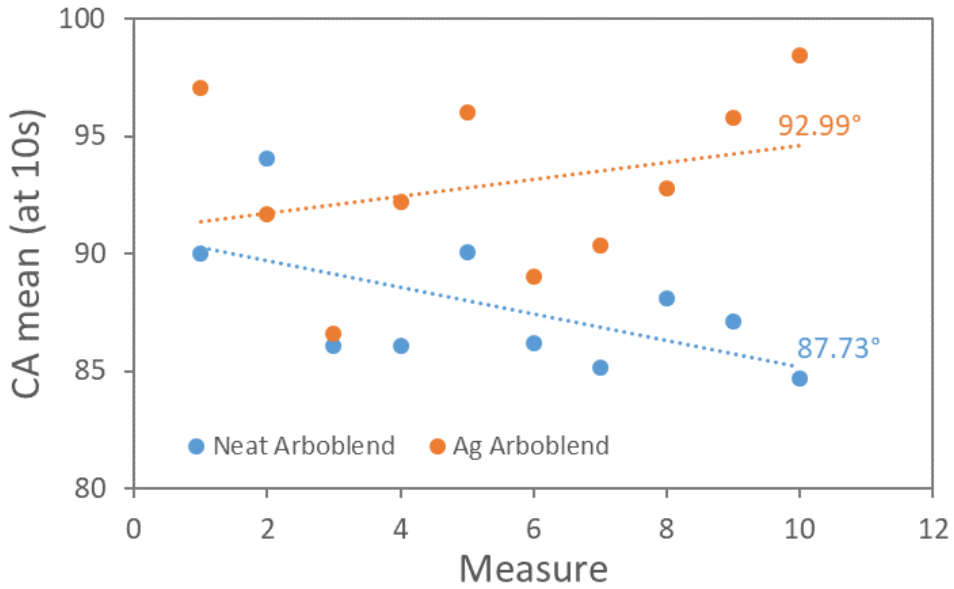


Fig. 7. CA values at 10s from drop deposition.

Conclusions

The oxygen barrier issue so present in food packaging it has a possible solution by using nano- technologies because of the very small amount of added material. It is applicable also in the case of PVD coatings with silver target, and Arboblend V2 Nature biodegradable polymer. Thus, less than 0.14 wt% of silver nanoparticles, [7,

10], is able to reduce the oxygen transmission ratio of the Arboblend V2 Nature sheets down to 32%. But, to increase shelf life of oxygen-sensitive foods it is also necessary to create a moisture barrier. Through contact angle measurements, sessile drop method, the Arboblend V2 + AgNP's pointed a weak wettability of the sheet surface, the wetting angle being more than 90°.Following the analysis of the obtained it can recommend the use in food industry applications (and not only) of sheets obtained from Arboblend V2 Nature +AgNP's due to their appropriate surface properties.

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