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Silver Nano-Coating of Liquid Wood for Nanocomposite Manufacturing

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Abstract

The green composites from renewable resources are being increasingly studied because of their potential to provide benefits to the natural environment. Biotechnologies such as liquid wood injection moulding have several merits into account. Liquid wood is a thermoplastic material made from byproducts of the wood pulp industry. The liquid wood is in the form of pellets, which for processing will be melted and injected, just like plastics. This study is set to explore the potential advantages of combining liquid wood with silver nanoparticles. The use of silver-nanoparticles as antimicrobial agent is being evaluated for biomedical devices as well as furniture in many public places. In order to solve manufacturing problems in handling and spreading nano-particles in injection moulding products, an innovative methodology has been used. Plastic pellets are coated by Physical vapor deposition (PVD) with a nanometric layer of metallic silver. This continuous nanofilm produces silver nanoparticles during the plastification stage of the injection moulding process. Nano-coating fragmentation allows to distribute silver nano-platelets in the polymer matrix with very low contents and incomparable homogeneity. PVD coating has been optimized to take into account the nature of the raw material to process, mainly in terms of high-water content and small pellet size. Differential scanning calorimetry (DSC) on liquid wood granules coated with silver showed that no alteration has been produced in PVD. In fact, DSC scans show that no interaction is present between the polymer structure and the metal coating. These studies allow also a preliminary evaluation of the properties belongs of the new biomaterial, while opening for discussion the potential applications and future use in a wide variety of areas such as: bioengineering, medical and others.

Keywords: Nanocomposites; Polymers; Silver nanoparticles; Liquid wood; Nano-coating

1. Introduction

This paper is set to expose the nano-coating of one type of liquid wood, called Arboblend V2 Nature with silver nanoparticles by Physical Vapor Deposition process. The present task is to develop nanocomposites with antibacterial properties. Silver nanoparticles are known to provide antimicrobial properties for surfaces. Because silver nanoparticles have been integrated into different applications for their antimicrobial influence, the properties with antibacterial role has been of great interest in recent years. Nanocomposites represents an innovative category of polymeric filled composites with sole mechanical, physical, thermal and processing properties. Due to the positive contribution and the results obtained in terms of performance, they are suitable for use in the aerospace, automotive, chemical, transport industries and so on [1]. They can be manufactured at low cost and could offer additional compensations on density and processing with respect to metals and polymeric composites presently used in the manufacture of parts for automotive applications [2].

Silver nanoparticles have been noted for inclusion in a wide variety of applications in biotechnology. The most important two properties of the silver nanoparticles are: optical and antibacterial. Silver-based compounds have been widely used since the 19th century in many antimicrobial applications [3].

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Silver is generally used in the form of a salt, silver nitrate, but it would be possible to obtain enhanced antimicrobial behavior if silver nanoparticles were used, since the surface area for the bacteria to be exposed to would be bigger. Furthermore, the higher potential of nanoparticles compared to silver ions can be explained by their ability to anchor and penetrate the cell wall, influencing the membrane structure and causing the cell death [4].

Liquid wood is prepared from lignin that represents a waste from the wood industry. Wood is divided into lignin, cellulose and hemicellulose. The development of the "liquid wood" is part of the work of a team of researchers from the Fraunhofer Institute for Chemical Technology (ICT) in Pfinztal (Germany). Liquid wood is considered by structure, shade and odour related to wood, and it has mechanical and physical properties that are positioned, as values, among those of wood, conventional composites and polymers. Due to its properties, liquid wood could be used to replace the current plastic goods. Green composites from renewable resources are being increasingly studied because of their potential to provide benefits to the natural environment. Biotechnologies such as liquid wood have several merits. Liquid wood is obtained by combining lignin with fine natural fibers extracted from wood, hemp or flax and natural additives such as wax. The liquid wood is in the form of granules, which for processing will be melted and injected (moulding process), just like plastics [5]. Three categories of "liquid wood" stand acknowledged: Arbofill, Arboblend and Arboform®. Being considered a green material, liquid wood has a highly appreciated feature, namely that it can be re-melted and reinjected several times without its properties being diminished [6]. Ever since lignin has been classified as a natural, renewable source with nearly no geographical constraint, it not only has the prospective to subordinate the environmental influence of petroleum production and processing, but as well to avoid conflicts ascending from geographical and quantitative restrictions of this resource [7]. The liquid wood know-how is adept of substituting plastic by providing mankind with innovative materials for numerous years forward. The weaknesses of liquid wood would remain its mass, being heavier than regular plastic materials, and the manufacturing costs, which are nearly twice than those of Polypropylene (PP), one of the most widely used plastic materials. Material branded as liquid wood present some worthy merits: they use renewing resources, have a controllable biodegradability, have a natural wood like appearance, have a reduced die contractibility, and even good acoustic properties. It looks like wood, feels like wood, is even made of wood, but it shifts shape and solidifies like plastic. Also, it can be manufactured on a mass scale as well as molded into any shape or form. As a mixture with "unsorted" fibers, liquid wood is an isotropic material, instead of the natural wood. Liquid wood has mechanical and physical properties which are situated, as values, among those of wood.

The paper is structured as follows: section 2 present the Arboblend V2 Nature material; section 3 reveals the silver nano-coating process; the 4th section details the results and discussions and, in the end, conclusions are drawn and future work is exposed.

2. Arboblend V2 Nature

At the base of the creation of biopolymers there is the natural process of photosynthesis: in fact, thanks to solar radiation, plants are able to transform carbon dioxide and atmospheric water, in addition to soil water, into organic material (biomass) from which goods such as paper or plastic can be obtained [10]. Being extracted from wood, lignin can be considered as a possible renewable source of antioxidants and decomposable and harmless stabilizers. From the studies reported so far that refer to the identification of the features of the materials essential for adapting the antioxidant and stabilizing effects of the different types of lignin, papers with substantial results have emerged [8, 9].

Arboblend® combines various material types. Depending on the formula, ARBOBLEND® materials contain biopolymers such as polyester (e.g. bio-PET), starch, polylactic acid (PLA), bio-polyolefins (bio-PE), bio-polyamides (bio-PA), lignin, natural resins, natural waxes, natural oils, natural fatty acids, cellulose, organic additives and natural reinforcing fibres. Arboblend® materials are designed to be biodegradable or resistant depending on the intended application. The list of applications of liquid wood is very extensive because this material fulfills the conditions of the two most utilized materials on the planet. It can be manufactured a vast category of objects from simple toys and figures to complex gadgets, disposable cups to long-lasting automobile parts, custom-cast furniture to heavy-duty helmets, decorative gift boxes, crayons, pencils and loudspeaker boxes. Some of the most popular specific applications of liquid wood are: Green Lantern - Politec Valtellina Product; Minimal Shelf - Magis Product; Eco Pump - Sergio Rossi for Gucci Product; The Zartan "liquid wood" chair; Siemens Envisions Green Phones; Toyota MOB electric car concept.

3. Silver nano-coating technique

Physical Vapor Deposition is one of the most used coating methods in industrial sector. Creating PVD coatings on non-metal materials is an unconventional approach, which is not very investigated. The process is based on releasing coated material from the source target and transferring it to the coated object surface, thus creating a thin film. The PVD sputtering equipment that was used for the silver nano-coating process, represented in Fig. 1, was manufactured by MITEC S.R.L. and had been previously used for other procedures.

Fig. 1. VS-40 MITEC PVD sputtering equipment

The vacuum chamber is a cylindrical stainless-steel chamber with a diameter of 450mm and a height of 600mm and a door for the insertion and extraction of the pellets to be coated. In order to gain a uniform layer on each pellet it was needed a handling system inside the chamber. For this reason, the system was modified by adding a rotating basket, involving a cylindrical container with horizontal rotating axis, connected to an electric motor and mounted on the chamber door. This system let to coat large number of pellets, since the rotation movement allows the direct exposure of all the pellets on their entire surface. The sputtering time is strictly related to the quantity of pellets, since increasing the number of pellets decreases the time of exposure to the target and more time is required to obtain the same coating thickness. The machine was equipped with three cathodes. Because of the rotating basket position, the central target was useless for the scope, whereas the two laterals could be used together or one per time. Regarding our experiment, one Silver target was allocated, having a rectangular shape (300x125) mm^2 and a purity of 99.99%. The chamber and the rotating basket are shown in Fig. 2, while in Fig. 3 is pointed out the position of the targets and the shutter that is used for keeping the Argon pressure in the chamber during the sputtering process.

Fig. 2. Sputtering chamber and basket used for handling the pellets

Fig. 3. Targets position and shutter inside the chamber

The machine is well described in Fig. 4, which shows a software package print screen of process chamber which is the basis of the equipment operation.

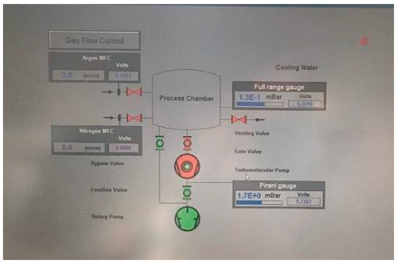

Fig. 4. Scheme of the PVD sputtering equipment

The vacuum in the chamber is obtained by means of a pre-vacuum rotary vane pump PFEIFFER BALZERS DUO 030A and a high vacuum turbomolecular pump PFEIFFER TMH 1601 (Fig. 5a, b). The rotary pump, having a power of 1.1 kW and a maximum suction flow of 30m^3/h, let to reach the pressure of 10^{-2}bar in the vacuum chamber. The turbomolecular pump is a high-vacuum pump having a functional scheme similar to a turbopump, whose works by giving momentum to gas molecules in a determined direction by continuous collisions with rotating vanes.

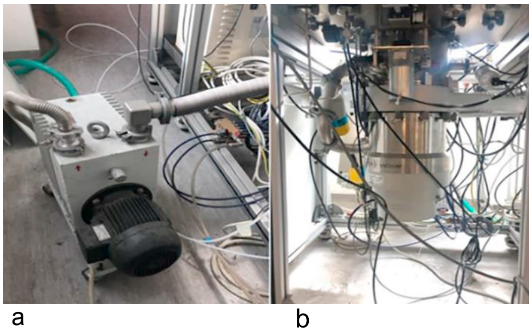

Fig. 5. Equipment used to obtain the vacuum: (a) Rotary vane pump Pfeiffer Balzers Duo 030A; (b) Turbomolecular pump Pfeiffer TMH 1601

Moreover, the system is equipped with an Argon tank, to be used as plasmogen process fluid and regulated by a flowmeter valve, and with a Nitrogen tank, used for the venting at the end of the process.

The PVD machine is also furnished with a cooler for chilling the system. Also, on the chamber door there is an eyelet used to facilitate visibility of the glow discharge and rotating basket represented in Fig. 6a, b.

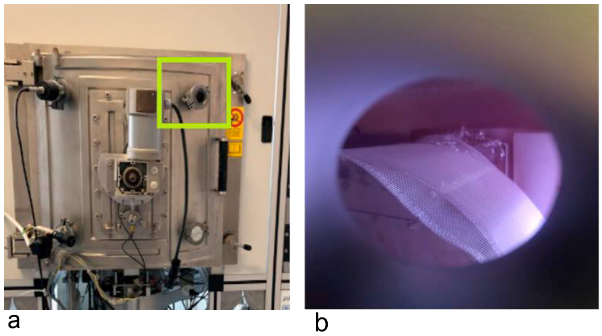

Fig. 6. The PVD machine parts: a) Position of the eyelet situated on the chamber door; b) Glow discharge and rotating basket seen from the eyelet during sputtering

For the pressure control, the machine is also equipped with a “Full range gauge”, in the process chamber, and a “Pirani gauge”, between the turbomolecular pump and the Foreline valve. Between the chamber and the gate valve, there is a shutter that must be kept open while reaching the sputtering pressure, whereas it has to be closed during the sputtering so as to hold back the Argon in the chamber without having to reduce the turbomolecular pump speed. A trap filter, allocated between the shutter and the gate valve, prevents solid particles to join the head of the turbomolecular pump.

Table 1. Test parameters for using the VS-40 PVD Sputtering Machine by MITEC for coating of ARBOBLEND V2 pellets with Silver nanoparticles.

Coating cycles	I	II	III	IV	V
DS Power	300W	330W	423W	430W	430W
Deposition time	40 min	30 min	30 min	30 min	30 min
Quantity of ARBOBLEND V2® pellets	278g	1388g	1388g	1388g	556g
Basket speed			23rpm		
Gas type			Argon		
The amount of gas			100 cm^3/min		
Power Intensity	1.41A	0.88A	1.02 A	1.03A	1.02A

4. Results and discussions

4.1. Degradation in the oven at 500°C of ARBOBLEND V2 (10 pellet/sample)

For the first step, were prepared 2 containers with pellets, one of them containing virgin granules and the other one, coated pellets with silver nanoparticles by the PVD process (Fig. 7a).

To perform this analysis, 6 ceramic containers were used in which 10 pellets of Arboblend V2 were introduced, both coated and virgin. Immediately after this test and the cooling were carried out, the containers were weighed, establishing the exact value of the remaining residues (Fig. 7b). The data obtained can be seen in Table 2. Also, Fig. 8 reveals our first test of nano-coating by PVD process using a small quantity of Arboblend V2, which was only 288g.

Table 2. Arboblend V2 Virgin versus Arboblend V2 Coated

			Before		
	Arboblend V2 Virgin			Arboblend V2 Coated	
No	Pellet	Pellet + Container	No	Pellet	Pellet + Container
1	261.0 mg	12.4098 g	4	260.7 mg	13.3820 g
2	268.5 mg	11.5652 g	5	261.5 mg	13.5864 g
3	236.5 mg	11.8098 g	6	256.4 mg	14.2676 g
			After		
	Arboblend V2 Virgin Waste			Arboblend V2 Coated Waste	
No	Pellet	Pellet + Container	No	Pellet	Pellet + Container
1	0.1 mg	12.1489 g	4	1.7 mg	13.1196 g
2	0.6 mg	11.2961 g	5	0.2 mg	13.3247 g
3	0.5 mg	11.5463 g	6	0.4 mg	14.0116 g

Fig. 7. Samples of virgin and coated Arboblend V2 pellets

Fig. 8. Nano-particles silver coating of Arboblend V2 sample

Consider that the melting temperature of Arboblend V2 pellets is 170°C, the quantity of silver nanoparticles couldn’t be determined by using this method.

4.2. DSC Test

DSC test as a thermal analysis is a powerful method to evaluate material properties such as glass transition temperature (Tg), melting, oxidation, crystallization and thermal stability. Also, DSC compares differences between the heat flow rate of the test sample and known reference material.

The DSC test was performed for both a sample of virgin material (Fig. 9) and a sample of material coated with silver nanoparticles (Fig. 10). The first curve is represented by green color and the 2nd with red color.

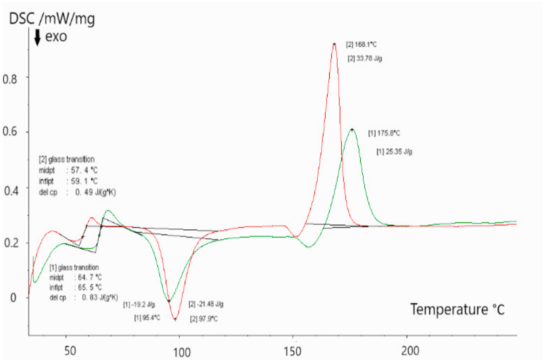

Fig. 9. DSC analysis for Arboblend V2 virgin material

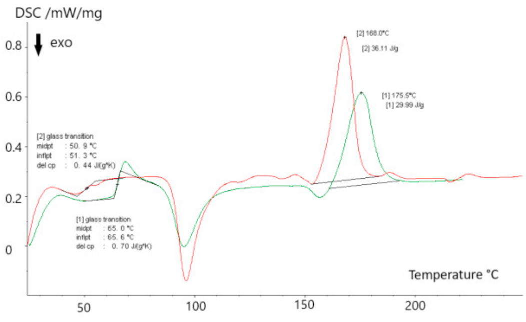

Fig.10. DSC analysis for Arboblend V2 coated with silver nanoparticles

DSC thermograms show two main specific wide and relatively flat peaks with gently sloping baseline. A glass transition temperature (Tg) of the lignin cannot be separated, being too indiscernible to be determined with reliability.

The DSC curve recorded during the heating of the Arboblend V2 Nature virgin material (Fig. 9) has two peaks up to 150°C: an endothermic peak occurs during heating from room temperature to 100°C and an exothermal peak of greater intensity occurs during heating to temperature exceeding 200°C. The deviation from linearity of the heat flow between two peaks suggests the presence of a solid-state endothermic transformation occurring upon heating.

Take into account the DSC curve for Arboblend V2 Nature coated with silver nanoparticles (Fig. 10) reveals the same tendencies as base material. This means no alteration has been produced in PVD process and the interaction is present between the polymer structure and the metal coating.

5. Conclusions

The purpose of this article is to point out that this new material made of liquid wood and silver nanoparticles will have both antibacterial and mechanical properties due to the alloying of these two unconventional materials.

The main experiment consists in two phase process: coating the liquid wood granules with silver nanoparticles and obtaining final products by injection moulding. As a first step, the liquid wood pellets were coated with a thin film of silver nanoparticles, and subsequently these granules obtained from the two unconventional materials will be processed using the same injection moulding machine on which the plastics work as a second step. The DSC recorded for base material Arboblend V2 Nature and coated with silver nanoparticles shows the same behavior during the heating process up to 200°C. This behavior constitutes very useful information for obtaining different parts using injection moulding because it means that there were no interactions between the base material and the metal coating. The parts obtained from the new material in the near future will be tested to accurately determine the mechanical, electrical, optical and others properties.

Future work

Combining liquid wood with silver nanoparticles is a promising direction of research which could unveil multiple results that could be put into practice by different areas. The main research goals of my future work will be centered on:

- Study of the mechanical properties (tensile strength, bending, impact, etc.) of the parts made from liquid wood coated with silver nanoparticles obtained by injection moulding;
- Thermal properties (DSC, EDAX etc) evaluation of parts made from liquid wood coated with silver nanoparticles obtained by injection moulding;
- Structure analysis (SEM) of the parts made from liquid wood coated with silver nanoparticles obtained by injection moulding;
- Study of tribological properties (coefficient of friction and wear);
- Identification of at least one landmark with industrial applicability.

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