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EXPERIMENTAL FACTORIAL PLAN FOR COATING BIODEGRADABLE MATERIALS WITH SILVER NANOPARTICLES

BY

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Abstract. This paper aims to present the development of new material with enhanced properties using a biodegradable material such as Arboblend V2 Nature and silver nanoparticles through Physical Vapor Deposition process. Thus, the materials chosen for this study are Arboblend V2 Nature and silver. Arboblend V2 Nature is a thermoplastic material made from byproducts of the wood pulp industry to replace plastic materials made from petroleum. Silver nanoparticles are known to provide antimicrobial properties for surfaces. Physical Vapor Deposition is one of the most used coating methods in the industrial sector. The main goal is to create a benchmark of materials that can be further exploited in a wide variety of applications in areas such as medical, dental, automotive, electronics, and others.

Keywords: experimental factorial plan; PVD; biodegradable materials; silver nanoparticles.

1. Introduction

Resources play a crucial role in providing value to society. Sustainable use of resources, both from natural and man-made sources, has received

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increasing attention in recent decades. There have been many proposals to direct production to new systems that are more sensitive to environmental issues. For the results to be tangible, the footprint of human activities on ecosystems must be less than the maximum limit they can withstand before they reach a condition of irreversible degradation. In principle, this result can be obtained through two antithetical orientations: one is based on non-interference, where the whole technological process is closed forming techno cycles; the other orientation focuses on the concept of biocompatibility which ensures the maximum integration of production with natural processes (biocycle). The main goal is to achieve systems based on renewable resources reintroduced into the ecosystem in the form of totally biodegradable waste. Following this orientation, the development of biopolymers has gained new impetus and vigor in recent years. These biodegradable materials have used in the past to produce rubbers such as gutta-percha, rubber, shellac, or even to produce cellophane, but they were "set aside" in favor of more petroleum-derived resins and synthetic polymers that are more advantageous in terms of production, performance, and costs. Fig. 1 shows a classification by origin of biodegradable plastics. Their dissemination and marketing are influenced by performance and costs. At the same time, they are influenced both by the low diffusion of these biopolymers on the market and by the price of oil affecting the production of synthetic plastics and, consequently, by the manufacturer's choice whether or not to target the biopolymers market. Currently, 99% of plastics come from non-renewable resources and are used both as raw material and as an energy source in the production process (4% of world oil production becomes plastic). The world currently consumes around 200 million tons of plastic per year (mainly in developed countries), with an outcome of over 25 million tons/year of plastic waste in Europe and the USA […].

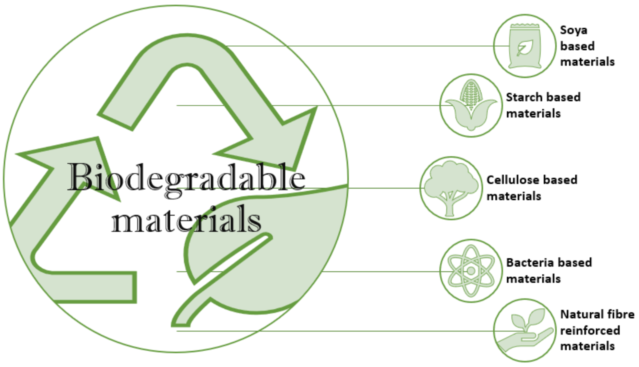

Fig. 1 – Classification of biodegradable materials.

All this involves problems of availability of raw material to produce plastics, difficulties related to the disposal of waste in the post-use phase. Renewable green composites are increasingly being studied because of their potential to provide benefits to the natural environment. Thus, lignin was mixed with several polymers to obtain materials for various high value-added applications. Efficient mixing is often difficult to achieve given the high complexity of the lignin structure and its reactivity. Lignin manifests a thermoplastic behavior due to its strong network of intra-molecular and inter-molecular hydrogen bonds (Sakakibara, 1980; Nimz, 1974), but at high temperatures, it acts as a heat-resistant material by the appearance of extensive crosslinking reactions (Culebras *et al*., 2018a; Kubo and Kadla, 2005). In this context, it is of critical importance to thoroughly investigate the miscibility of lignin with other polymers, to monitor the evolution of phases, because their compatibility is of real importance to understand the structure-property relationships of lignin-based mixtures (Sen *et al*., 2015). To obtain better properties in lignin-polymer mixtures, chemical modification of lignin is often necessary (Alexy *et al*., 2004; Sailaja and Deepthi, 2010; Blanco *et al*., 2017; Gordobil *et al*., 2015; Barzegari *et al*., 2012; Wei *et al*., 2006; Kaewtatip and Thongmee, 2013). Usually, lignin, pure or chemically modified, can be used to perform the following functions in a mixing system: reactive component in the preparation of various resins (eg epoxy resins, phenol-formaldehyde resins (Wang *et al*., 2009; Tachon *et al*., 2016) and polymers (for example polyurethanes (Culebras *et al*., 2018b; Lee and Deng, 2015; Bernardini *et al*., 2015; Jia *et al*., 2015), nuclear agent (Perez-Camargo *et al*., 2015; Weihua *et al*., 2004; Lin *et al*., 2011; Mu *et al*., 2014), surfactant (Zhou *et al*., 2015; Gupta and Washburn, 2014), UV blocker (Gregorova *et al*., 2005; Xing *et al*., 2017), thermal stabilizer (Kabir *et al*., 2018; Kabir, 2018; Ye *et al*., 2018; Barana *et al*., 2016), flame retardant (Liu *et al*., 2016a, b), adsorbent (Albadarin *et al*., 2017), composite reinforcement filler (Benjelloun-Mlayah and Delmas, 2014; Kosikova and Gregorova, 2005), antimicrobial agent (biocide) (Erakovic *et al*., 2014), supercapacitor for energy storage (Peng *et al*., 2018; Ho *et al*., 2018), carrier (for biomedical and pharmaceutical applications) (Farhat *et al*., 2017) and precursor for sustainable and cost-effective carbon fibers (Mainka *et al*., 2015). This paper is structured as follows: the first part presents some preliminary notions as an introduction about biopolymers and biodegradable materials based on lignin; the second part is dedicated to the general presentation of the materials used for the experimental plan; in the third part the vapor deposition equipment (PVD) is described and the fourth section is represented by the experimental factorial plan.

2. Description of Materials Used for Experiments

Liquid wood is made from lignin, which is a waste product from the wood pulp industry, and is in the form of granules, which for processing can be melted and injected (molding process). The main types of liquid wood are: Arboblend®, Arbofill® and Arboform® (Fig. 2).

(a) Arboblend V2® sample (b) Arboform LV3® sample

(c) Arboform F40® sample (d) Arbofill® sample

Fig. 2 – Different types of liquid wood.

Arboblend V2 Nature

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

Arboform LV3®

This liquid wood version consists of a lignin matrix (60%) enriched with a good percentage of lignin loaded with flax or hemp fibers (40%). At first sight, cellulose gives it a light brown color and a slightly rough surface. Thanks to these characteristics, it is possible to produce artifacts with more natural appearances, which therefore represent a step following the purely substitutive use seen in the Arboblend®, enhancing properties not obtainable with traditional polymers. Furthermore, the filler improves the mechanical properties, making the material more rigid.

Arboform F40®

This third sample of material contains more cellulose (60%) than the two already described; it can therefore be imagined that it is the one that most differs from a plastic and more recalls the idea of wood. In addition to the dark brown color and the blotchy nuances that form once printed, the material has an easily noticeable smell; everything immediately recalls its natural origin.

Arbofill®

Unlike other types of liquid wood, Arbofill® is made up of petrochemical polymers such as polyethylene or reinforced polypropylene, mixed with natural fibers such as hemp, linen, or wood. By modulating the polymeric component, different types of Arbofill can be obtained based on the needs of the individual customer and the purpose of using the material. This product is also completely recyclable and has the appearance of a light wood. The list of liquid wood applications is extensive. A wide range of items can be manufactured, from simple toys and figures to complex items, disposable glasses to long-lasting car parts, furniture parts, to durable headphones, decorative boxes, pencils, and speaker boxes.

The research team within the Gheorghe Asachi Technical University of Iași, Department of Machine Building Technology, has conducted numerous studies and research on determining the mechanical, thermal, and structural properties of liquid wood parts obtained by injection molding, (Nedelcu *et al*., 2013; Nedelcu, 2013; Nedelcu *et al*., 2016; Nedelcu and Comaneci, 2014; Nedelcu *et al*., 2015; Broitman *et al*., 2018; Nedelcu and Paunoiu, 2015; Mazurchevici *et al*., 2018; Plavanescu *et al*., 2015; Nedelcu *et al*., 2019; Plavanescu *et al*., 2016; Motaş *et al*., 2020; Motaş and Nedelcu, 2019; Nedelcu *et al*., 2014). These properties need to be known to carry out the coating process with silver nanoparticles in good condition.

Silver is the metal that has attracted interest to produce metallic nanoparticles, due to its well-known antibacterial properties. Silver-based compounds have been widely used since the 19th century in many antimicrobial applications. The use of silver nanoparticles as an antimicrobial agent is evaluated for biomedical devices as well as for furniture in many public places (stations, elevators, and so on). Silver ions are highly toxic to all 16 major bacterial species (Gadd *et al*., 1989). Silver is generally used in the form of salt, silver nitrate, but it would be possible to obtain an improved antimicrobial behavior if silver nanoparticles were used because the surface to which the bacteria will be exposed would be larger. Moreover, the higher potential of nanoparticles compared to silver ions can be explained by their ability to anchor and penetrate the cell wall, influencing the structure of the membrane and causing cell death (Prabhu and Poulose, 2012). Silver nanoparticles have attracted tremendous interest in the biomedical field due to their attractive and unique nano-related properties, including their high intrinsic antimicrobial efficacy and non-toxic nature. Among the many potential applications of silver nanoparticles in this field, impressive attention and effort have recently been directed to their promising implications in wound dressing, tissue scaffolding, and protective clothing applications (Mokhena and Luyt, 2017; Gudikandula *et al*., 2017). Some key issues related to the specific antimicrobial characteristics of silver nanoparticles involve their intrinsic physical and chemical properties, which include maintaining the nanoscale size of silver nanoparticles, improving their dispersion and stability, and avoiding aggregation (Guan *et al*., 2018). Many studies have shown experimentally that the antipathogenic activity of silver nanoparticles are better than that shown by silver ions (Li *et al*., 2017).

3. Description of PVD Equipment

As is known, PVD spraying belongs to the family of physical vapor deposition techniques, which are widely used for the deposition of thin films on a substrate, to improve the physical and chemical properties of materials. This technique, which is now known as "Sputtering - PVD", requires a high vacuum and a bright discharge (plasma). In the spraying process, the physical vaporization of the atoms on the target surface takes place by bombarding it with energetic ions, and the resulting impulse transfer to the target atoms. Energy ions come from ionized gas in an electric field. Gas pressure plays an important role in plasma formation. If the gas pressure is very low, only the ions resulting from the natural radiation will be transferred to the poles. In the presence of higher pressure, natural ions are accelerated, and their collisions lead to the generation of other ions and the increase in current. The spraying process can be used for alloys and mixtures with the advantage of having the same target composition in the coating. Being the target in a solid-state, there is no diffusion when it is bombarded by ions and each layer of atoms must be removed from the surface before the next layer can be sprayed. Fig. 3 shows the parts of physical vapor deposition (PVD) equipment.

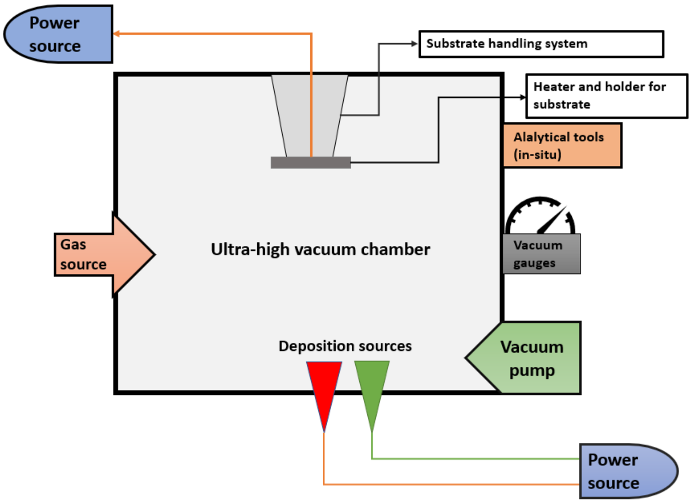

Fig. 3 – The main parts of a PVD equipment.

Like any surface treatment technology, the PVD process is used to impart superior properties to the substrate. PVD makes it possible to deposit a multitude of materials (metals, oxides, nitrides, carbides, mixtures, conductors, insulators). The strictest condition for substrates is that they be compatible with the vacuum. The coatings are deposited atom by atom and can be very thin (thickness about 20 nm) and reliably deposited. PVD finishes add beauty to the finished piece, so it is often used in decorative products. Moreover, it provides corrosion resistance for applications with high humidity and protects against chipping, discoloration, or sanding. Fig. 4 shows the equipment used to coat Arboblend V2 Nature granules with silver nanoparticles.

Fig. 4 – VS-40 equipment manufactured by MITEC for the physical vapor deposition (PVD) process.

The vacuum chamber has a cylindrical shape made of stainless steel, with a diameter of 450 mm and a height of 600 mm, equipped with an access door that allows the insertion and removal of objects before and immediately after the coating process, Fig. 5.

Fig. 5. The vacuum chamber of the PVD machine

The sputtering process, after achieving the high-vacuum pressure in the chamber, includes the following steps:

- Closing the shutter (for maintaining the Argon inside the chamber);
- Opening the Argon flow valve, the flow control should be set at its maximum value (100 sccm), until the pressure inside the chamber reaches a settled and firm value;
- Turning on the power for starting the sputtering: the correct ignition of the plasma can be verified by an eyelet located on the chamber door;
- Turning off the power, after the sputtering time has expired;
- Closing the Argon flow valve;
- Opening the shutter;
- Closing the Gate valve (the foreline valve must be maintained in open position for avoiding the pressure at the tail of the turbomolecular pump to increase);
- Opening the venting valve until the atmospheric pressure in the chamber is reached and it is possible to open the door and extract the coated products.

The handling system motion should be turned on during the pre-vacuum step, as it helps for degassing the granules. The PVD machine is also furnished with a cooler for chilling the system.

4. The Experimental Factorial Plan

To achieve the proposed experimental plan, two types of materials were used, namely: Arboblend V2 Nature granules (4998 g) and a silver source. Fig. 6 shows Arboblend V2 Nature granules before and after silver coating, designed for injection molding, blow molding, extrusion, press casting and calendering (density = 1.30 g/cm^3). The granules were supplied by Tecnaro GmbH (Germany). A silver source with a purity of 99.99% (density = 10.49 g/cm^3). Designed for the physical deposition process - Sputtering was provided by the University of Rome "Tor Vergata" (Italy), Fig. 7.

a *b*

Fig. 6 – Arboblend V2 Nature granules: *a*) before coating, *b*) after the coating process.

Fig. 7 – The silver source used for the nano-coating of the granules of Arboblend V2 Nature.

Factor experiments analyze the effects of several input factors on the output response of a process. Factorial experimental planning is a method that establishes the values of input parameters and the number of experiments needed to analyze the influence of these parameters on the output response. Based on the experimental factorial plan, the experiments are performed that will generate the output response (s).

It is important to note that in addition to the "main effects", the factors may also result in "effects of their interactions".

In the present paper, three input factors were considered: A-thickness of the deposited silver layer, B-rotation speed of the PVD equipment tank, and C-amount of coated material, each factor having two levels of variation.

The three factors, each on two levels (0 and 1), generate a factorial experiment 23, eight experiments will result ($2^3=8$), Table 1, (Batra and Seema, 2019; Academia Edu, 2019):

Table 1

The Factorial Experiment 2^3 with Two Levels of Variation

Test	Feedback experiment	A	B	C
1	(1)	0	0	0
2	a	1	0	0
3	b	0	1	0
4	ab	1	1	0
5	c	0	0	1
6	ac	1	0	1
7	bc	0	1	1
8	abc	1	1	1

The calculation ratios of the effects are according to Eqs. (1 - 3):

The effect of factor A:

$$A=\frac{1}{4}\{[abc]-[bc]+[ac]-[c]+[ab]-[b]+[a]-[1]\}=\frac{1}{4}(a-1)(b+1)(c+1) \quad (1)$$

The effect of the interaction of factor A with factor B:

$$AB=\frac{1}{4}[(abc)-(bc)-(ac)+(c)-(ab)-(b)-(a)+(1)] \quad (2)$$

The effect of the interaction of the three factors:

$$ABC=\frac{1}{4}[(abc)-(bc)-(ac)+(c)-(ab)+(b)+(a)-(1)] \quad (3)$$

or equivalent, Eqs. (4) and (5):

$$AB=\frac{1}{4}(a-1)(b-1)(c+1) \quad (4)$$

$$ABC=\frac{1}{4}(a-1)(c-1)(c-1) \quad (5)$$

A graphical representation of the complete three-factor experiment can also be made according to Fig. 8.

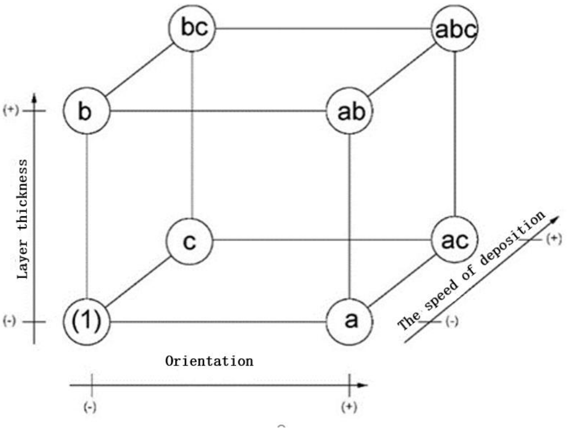

Fig. 8 – Geometrical model of the 2^3 factorial plan,
(Batra and Seema, 2019; Apio, 2019).

In this paper, only the interactions between every two factors were considered and the interaction between all three factors was eliminated because the resulting system with the 8 experimental values would be indeterminate to calculate the constants, coefficients, and error of the model.

The paper also used the MiniTab application and went through the following steps:

- Introduction of the values observed from performing the experiments;
- Consideration of the model of the three factors (A, B, C) and with the three interactions (AB, BC, and CA);
- Analysis of the variance of the factors and obtaining the constant and the coefficients of the generalized linear model.
- Elimination from the model of factors and interactions with statistically insignificant influence from the generalized linear model.
- Analysis of the variance of the factors and obtaining the constant and the coefficients of the new generalized linear model.
- Hierarchy of factors and their interactions according to the influence exerted on the response followed by the experiment. Highlighting the meaning of influences - whether they are directly proportional or inversely proportional to the response.

Finally, the two levels for the three input factors are shown in Table 2, which shows the complete factorial plan used to coat Arboblend V2 Nature granules with silver nanoparticles.

Table 2

Full Experimental Plan

Nr. Exp.	Input parameters		
	The silver layer thickness	The motion speed of the PVD handling system	The quantity of nano-coated granules
1	-1	-1	-1
2	-1	-1	+1
3	-1	+1	-1
4	-1	+1	+1
5	+1	-1	-1
6	+1	-1	+1
7	+1	+1	-1
8	+1	+1	+1

5. Conclusions

In the present work, the experimental factorial plan was made to cover the Arboblend V2 Nature granules with silver nano particles. Also, a comprehensive introduction was made with the general presentation of information related to biodegradable materials based on lignin and silver particles but also a general description of the equipment that will be used for coatings on the PVD principle. In the final part is presented the experimental factorial plan with the specification of the three input factors and the levels of variation. From the experience of the research team, it was considered that the factors of the thickness of the deposited silver layer, the rotation speed of the tank of the PVD equipment and the amount of coated material can have a significant influence on the output responses.

REFERENCES

Albadarin A., Collins M., Naushad M., Shirazian S., Walker G., Mangwandi C., *Activated Lignin-Chitosan Extruded Blends for Efficient Adsorption of Methylene Blue*, Chemical Engineering Journal, **307**, 264-272 (2017).

Alexy P., Kosikova B., Crkonova G., Gregorova A., Martis P., *Modification of Lignin-Polyethylene Blends with High Lignin Content Using Ethylene-Vinylacetate Copolymer as Modifier*, Applied Polymer Science, **94**, 1855-1860 (2004).

Barana D., Ali S., Salanti A., Orlandi M., Castellani L., Hanel T., Zoia L., *Influence of Lignin Features on Thermal Stability and Mechanical Properties of Natural Rubber Compound*s, ACS Sustain. Chem. Eng., **4**, 5258-5267, 2016.

Barzegari M., Alemdar A., Zhang Y., Rodrigue D., *Mechanical and Rheological Behavior of Highly Filled Polystyrene with Lignin*, Polymer Composites, **33**, 353-361, 2012.

Batra P.K., Seema Jaggi, *Factorial Experiments*, https://www.coursehero.com/file/9170119/5-Factorial-Expts/, accessed on 09.08.2019.

Benjelloun-Mlayah B., Delmas M., *Use of a Lignin for the Mechanical Reinforce- Ment of Elastomers, and Elastomer Thus Strengthened*, Tech. Rep., 2014.

Bernardini J., Cinelli P., Anguillesi I., Coltelli M.-B., Lazzeri A., *Flexible Polyurethane Foams Green Production Employing Lignin or Oxypropylated Lignin*, European Polymer Journal, **64**, 147-156 (2015).

Blanco I., Cicala G., Latteri A., Saccullo G., El-Sabbagh A., Ziegmann G., *Thermal Characterization of a Series of Lignin-Based Polypropylene Blends*, Journal of Thermal Analysis and Calorimetry, **27**, 147-153 (2017).

Broitman E., Nedelcu D., Mazurchevici S., Glenat H., Grillo S., *Tribological and Nanomechanical Behavior of Liquid Wood*, Journal of Tribology, **141**, *2* (2018).

Culebras M., Beaucamp A., Wang Y., Clauss M., Frank E., Collins M., *Biobased Structurally Compatible Polymer Blends Based on Lignin and Thermoplastic Elastomer Polyurethane as Carbon Fiber Precursors*, ACS Sustain. Chem. Eng., **6**, 8816-8825 (2018a).

Culebras M., Sanchis M., Beaucamp A., Carsi M., Kandola B., Horrocks A., Panzetti G., Birkinshaw C., Collins M., *Understanding the Thermal and Dielectric Response of Organosolv and Modified Kraft Lignin as a Carbon Fire Precursor*, Green Chemistry, **19**, 4461-4472 (2018b).

Erakovic S., Jankovic A., Tsui G., Tang C.-Y., Miskovic-Stankovic V., Stevanovic, T., *Novel Bioactive Antimicrobial Lignin Containing Coatings on Titanium*

Obtained by *Electrophoretic Deposition*, Int. J. Mol. Sci., **15**, 12294-12322 (2014).

Farhat W., Venditti R., Mignard N., Taha M., Becquart F., Ayoub A., *Polysaccharides and Lignin-Based Hydrogels with Potential Pharmaceutical Use as a Drug Delivery System Produced by a Reactive Extrusion Process*, Int. J. Biol. Macromol., **104**, 564-575 (2017).

Gadd G., Laurence O., Briscoe P., Trevors J., *Silver Accumulation in Pseudomonas Stutzeri AG259*, Biology of Metals, **2**, 168-173 (1989).

Gordobil O., Delucis R., Egues I., Labidi J., *Kraft Lignin As Filler in PLA to Improve Ductility and Thermal Properties*, Industrial Crops and Products, **72**, 46-53 (2015).

Gregorova A., Cibulkova Z., Kosikova B., Simon P., *Argyropoulos, Toward Thermoplastic Lignin Polymers; Part II: Thermal Polymer Characteristics of Kraft Lignin Derivatives*, Polymer Degradation and Stability, **89**, 553-558 (2005).

Guan Q., Xia C., Li W., *Bio-Friendly Controllable Synthesis of Silver Nanoparticles and their Enhanced Antibacterial Property*, Catalysis Today, **327**, 196-202 (2018).

Gudikandula K., Vadapally P., Singara Charya M., *Biogenic Synthesis of Silver Nanoparticles from White Rot Fungi: Their Characterization and Antibacterial Studies*, Open Nano, **2**, 64-78 (2017).

Gupta C., Washburn N., *Polymer-Grafted Lignin Surfactants Prepared via Reversible Addition-Fragmentation Chain-Transfer Polymerization*, Langmuir, **30**, 9303-9312 (2014).

Ho H., Nguyen N., Meek K., Alonso D., Hakim S., Naskar A., *A Solvent- Free Synthesis of Lignin-Derived Renewable Carbon with Tunable Porosity for Supercapacitor Electrodes*, Chem Sus Chem., **11**, 2953-2959 (2018).

Jia Z., Lu C., Zhou L., Wang P., *Preparation and Characterization of High Boiling Solvent Lignin-Based Polyurethane Film with Lignin as the Only Hydroxyl Group Provider*, RSC Advances, **5**, 53949-53955 (2015).

Kabir A., *Effects of Lignin as a Stabilizer or Antioxidant in Polyolfins*, in Electronic Thesis and Dissertation Repository the University of Western Ontario, Canada, 2018.

Kabir A., Yuan Z., Kuboki T., Xu C., *De-Polymerization of Industrial Lignins to Improve the Thermo-Oxidative Stability of Polyolfins*, Industrial Crops and Products, **120**, 238-249 (2018).

Kaewtatip K., Thongmee J., *Effect of Kraft Lignin and Esterified Lignin on the Properties of Thermoplastic Starch*, Materials Design, **49**, 701-704 (2013).

Kosikova B., Gregorova A., *Sulfur-Free Lignin as Reinforcing Component of Styrene-Butadiene Rubber*, Journal of Applied Polymer Science, **97**, 924-929 (2005).

Kubo S., Kadla J., *Hydrogen Bonding in Lignin: A Fourier Transform Infrared Model Compound Study*, Biomacromolecules, **6**, 2815-2821 (2005).

Lee A., Deng Y., *Green Polyurethane from Lignin and Soybean Oil Through Nonisocyanate Reactions*, European Polymer Journal, **63**, 67-73 (2015).

Li W., Sun T., Zhou S., Ma Y., Shi Q.-S., Xie X., Huang X.-M., *A Comparative Analysis of Antibacterial Activity, Dynamics, and Effects of Silver Ions and Silver Nanoparticles Against Four Bacterial Strains*, International Biodeterioration & Biodegradation, **123**, 304-310 (2017).

Lin N., Fan D., Chang P., Yu J., Cheng X., Huang J., *Structure and Properties of Poly (Butylene Succinate) Filled With Lignin: A Case of Lignosulfonate*, Journal of Applied Polymer Science, **121**, 1717-1724 (2011).

Liu L., Huang G., Song P., Yu Y., Fu S., *Converting Industrial Alkali Lignin to Biobased Functional Additives for Improving Fire Behavior and Smoke Suppression of Polybutylene Succinate*, ACS Sustain. Chem. Eng., **4**, 4732-4742 (2016).

Liu L., Qian M., Song P., Huang G., Yu Y., Fu S., *Fabrication Of Green Lignin-Based Flame Retardants For Enhancing The Thermal And Fire Retardancy Properties of Polypropylene/Wood Composites*, ACS Sustain. Chem. Eng., **4**, 2422-2431 (2016).

Mainka H., Tager O., Korner E., Hilfert L., Busse S., Edelmann F., Herrmann A., *Lignin - An Alternative Precursor for Sustainable and Cost-Effective Automotive Carbon Fiber*, J. Mater. Res. Technol., **4**, 283-296 (2015).

Mazurchevici S., Quadrini F., Nedelcu D., *The Liquid Wood Heat Flow and Material Properties as a Function of Temperature*, Materials Research Express, **5**, *3*, 035303 (2018).

Mokhena T., Luyt A., *Electrospun Alginate Nanoparticles Impregnated with Silver Nanoparticles: Preparation, Morphology and Antibacterial Properties*, Carbohydr. Polym., **165**, 304-312 (2017).

Motaş J.G., Nedelcu D., *Challenges with Developing Antimicrobial Bio-Materials by Combining Liquid Wood and Silver Nanoparticles*, 2019 E-Health and Bioengineering Conference (EHB), 1-4, 2019.

Motaş J.G., Quadrini F., Nedelcu D., *Silver Nano-Coating of Liquid Wood for Nanocomposite Manufacturing*, Procedia Manufacturing, **47**, 974-979 (2020).

Mu C., Xue L., Zhu J., Jiang M., Zhou Z., *Mechanical and Thermal Properties of Toughened Poly (L-Lactic) Acid and Lignin Blends*, BioResources, **9**, 5797-5815 (2014).

Nedelcu D., Ciofu C., Lohan N.M., *Microindentation and Differential Scanning Calorimetry of "Liquid Wood"*, Composites Part B: Engineering, **55**, 11-15 (2013).

Nedelcu D., Comaneci R., *Microstructure, Mechanical Properties and Technology of Samples Obtained by Injection from Arboblend V2 Nature*, NISCAIR-CSIR, India, 2014.

Nedelcu., D., *Investigation on Microstructure and Mechanical Properties of Samples Obtained by Injection from Arbofill*, Composites Part B: Engineering, **47**, 126-129 (2013).

Nedelcu D., Lohan N.M., Volf I., Comaneci R., *Thermal Behaviour and Stability of The Arboform® LV3 Nature Liquid Wood*, Composites Part B: Engineering, **103**, 84-89 (2016).

Nedelcu D., Marguta A., Mazurchevici S., Munteanu C., Istrate B., *Micro-Structural and Morphological Analyses of Coated 'Liquid Wood' Samples by Ceramic Particles*, Materials Research Express, **6**, *8*, 085326 (2019).

Nedelcu D., Paunoiu V., *Study of Microstructure and Mechanical Properties of Injection Molded Arboform Parts*, NISCAIR-CSIR, India, 2015.

Nedelcu D., Plavanescu S., Puiu E., *Impact Resistance of "Liquid Wood"*, Advanced Materials Research, 1036, 13-17, 2014.

Nedelcu D., Santo L., Santos A.G., Plavanescu S., *Mechanical Behaviour Evaluation of Arboform Material Samples by Bending Deflection Test*, Materiale Plastice, **52,** *4*, 423-426 (2015).

Nimz H., *Beech Lignin - Proposal of a Constitutional Scheme*, Agenwandte Chemie International Edition, **13**, 313-321 (1974).

Peng Z., Zou Y., Xu S., Zhong W., Yang W., *High-Performance Biomass-Based in Flexible Solid-State Supercapacitor Constructed of Pressure-Sensitive Lignin-Based and Cellulose Hydrogels*, ACS Appl. Mater. Interfaces, **10**, 22190-22200 (2018).

Perez-Camargo R., Saenz G., Laurichesse S., Casas M., Puiggali J., Averous L., Muller A., *Nucleation, Crystallization, and Thermal Fractionation of Poly (ϵ-Caprolactone)-Grafted-Lignin: Effects of Grafted Chains Length and Lignin Content*, Journal of Polymer Science, Part B, Polymer Physics, **53**, 1736-1750 (2015).

Plavanescu Mazurchevici S., Nedelcu D., Bellisario D., Carausu C., *Surface Analyses of Arboform Samples*, Key Engineering Materials, **699**, 80-85 (2016).

Plavanescu S., Quadrini F., Nedelcu D., *Tensile Test for Arboform Samples*, ACTA Universitatis Cibiniensis, **66**, *1*, 147-152 (2015).

Prabhu S., Poulose E., *Silver Nanoparticles: Mechanism of Antimicrobial Action, Synthesis, Medical Applications, and Toxicity Effects*, International Nano Letters, **32**, 2-10 (2012).

Sailaja R., Deepthi M., *Mechanical and Thermal Properties of Compatibilized Composites of Polyethylene, Esterin and Lignin*, Materials Design, **31**, 4369-4379 (2010).

Sakakibara A., *A Structural Model of Softwood Lignin*, Wood Science and Technology, **14**, 89-100 (1980).

Sen S., Patil S., Argyropoulos D., *Thermal Properties of Lignin in Copolymers, Blends, and Composites: A Review*, Green Chemistry, **17**, 4862-4887 (2015).

Tachon N., Benjelloun-Mlayah B., Delmas M., *Organosolv Wheat Straw Lignin as a Phenol Substitute for Green Phenolic Resins*, BioResources, **11**, 5797-5815 (2016).

Wang M., Leitch M., Xu C., *Synthesis of Phenol-Formaldehyde Resol Resins Using Organosolv Pine Lignins*, European Polymer Journal, **45**, 3380-3388 (2009).

Wei M., Fan L., Huang J., Chen Y., *Role of Star-Like Hydroxylpropyl Lignin in Soy Protein Plastics*, Macromolecular Materials and Engineering, **291**, 524-530 (2006).

Weihua K., He Y., Asakawa N., Inoue Y., *Effect of Lignin Particles as a Nucleating Agent on Crystallization of Poly(3-Hydroxybutyrate)*, Journal of Applied Polymer Science, **94**, 2466-2475 (2004).

Xing Q., Ruch D., Dubois L., Wu P., Wang W.-J., *Biodegradable and High-Performance Poly (Butylene Adipate-co-Terephthalate)- Lignin UV-Blocking Films,* ACS Sustain. Chem. Eng., **5**, 10342-10351 (2017).

Ye D., Kong J., Gu S., Zhou Y., Huang C., Xu W., Zhang X., *Selective Aminolysis of Acetylated Lignin: Toward Simultaneously Improving Thermal-Oxidative Stability and Maintaining Mechanical Properties of Polypropylene*, Int. J. Biol. Macromol., **108**, 775-781 (2018).

Zhou M., Wang W., Yang D., Qiu X., *Preparation of a New Lignin Based Anionic/Cat-Ionic Surfactant and Its Solution Behavior*, RSC Advances, **5**, 2441-2448 (2015).

http://www.apio.ro/upload/mc08_modele_exp_quasiexp.pdf, accessed on 09.08.2019.

https://www.academia.edu/19306213/Analiza_factorial%C4%83, accessed on 09.08.2019.

Tecnaro website, Available online: http://www.tecnaro.de/en/arboblend-arbofillarboform/, accessed on 15 December 2019.

PLANUL EXPERIMENTAL FACTORIAL PENTRU ACOPERIREA MATERIALELOR BIODEGRADABILE CU NANOPARTICULE DE ARGINT

(Rezumat)

Această lucrare își propune să prezinte dezvoltarea de noi materiale cu proprietăți îmbunătățite folosind un material biodegradabil, cum ar fi Arboblend V2 Nature și nanoparticule de argint, prin procesul de depunere fizică a vaporilor. Astfel, materialele alese pentru acest studiu sunt Arboblend V2 Nature și argint. Arboblend V2 Nature este un material termoplastic fabricat din subproduse din industria celulozei din lemn pentru a înlocui materialele plastice realizate din petrol. Se cunoaște că nanoparticulele de argint oferă proprietăți antimicrobiene pentru suprafețe. Depunerea fizică a vaporilor este una dintre cele mai utilizate metode de acoperire în sectorul industrial. Scopul principal este de a obține materiale acoperite cu argint care pot fi exploatate în continuare într-o mare varietate de aplicații în domenii precum medicale, stomatologice, auto, electronice și altele.