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1

INTRODUCTION

In recent years, modern technologies have allowed the study of materials at the nano level and thus helped to improve the properties of some materials by introducing small amounts of material into the matrix of another material to obtain by alloying a category of materials with superior properties called nanocomposites. This book presents the steps taken to obtain a new material with improved properties, obtained by combining two completely different materials, namely a biopolymer called Arboblend V2 Nature and silver nanoparticles, using a Physical Vapor Deposition - Sputtering deposition process. Arboblend V2 Nature is a thermoplastic material made from byproducts of the wood pulp industry to replace plastic materials made from petroleum that are harmful for the environment. Silver nanoparticles are well-known to provide antimicrobial properties for surfaces. Physical Vapor Deposition is one of the most used coating methods in industrial sector. The main goal was to create a benchmark of materials which can be further exploited in a wide variety of applications in areas such as: medical, dental, automotive, electronics and so on. The green composites from renewable resources are being increasingly studied because of their potential to provide benefits to the natural environment. As a consequence of the severe limitation of the natural reserves of the world, usable in the industrial expansions and due to the increasing requirement to preserve the functional parameters of the natural ecosystems, several worldwide agreements aim at increasing waste recycling and reuse, in this manner, gradually reducing the exploitation of natural resources. The biopolymer is in the form of granules, which for processing will be melted and injected (injection moulding process), similar with plastics. Lignin has been blended with a number of polymers in order to obtain materials for high added-value applications. The potential advantages of combining Arboblend V2 Nature with silver nanoparticles are undergoing continuous study and evaluation to identify future directions of application. Additionally, owing to their broad-spectrum antimicrobial ability, silver nanoparticles have also become the most widely used sterilizing nanomaterials in consuming and medical products, for instance, textiles, food storage bags, refrigerator surfaces, and personal care products. In order to solve manufacturing problems in handling and spreading nano-particles in injection moulding products, an innovative methodology has been used. The Arboblend V2 Nature 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. Uniform dispersion of nanoparticles in the polymer matrix leads to a significant improvement in the properties of the nanocomposites. 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. The main research project consists of the three-phase process:

- the first step includes coating Arboblend V2 Nature granules with silver nanoparticles by physical vapor deposition (PVD) – pulverization.
- the second step refers to the injection molding of Arboblend V2 Nature granules subsequently coated with silver and the obtaining of test-type parts;
- the last step is the compression moulding of both silver-coated Arboblend V2 Nature granules and uncoated granules.

Between the first and the second step, we performed the Direct Scanning Calorimetry (DSC) analysis, Degradation in the oven test, Scanning Electron Microscopy (SEM), X-ray photoelectron spectroscopy (XPS), and Nanoindentation. The second technology we used to obtain parts by alloying the two materials, namely Arboblend V2 Nature and silver, is injection molding. With the help of this procedure, we obtained test-type parts on which both mechanical tests and various thermal and surface tests and analyzes were performed, such as: Tensile/Impact/Bending test, Dynamic mechanical analysis (DMA), Direct Scanning Calorimetry (DSC), Thermogravimetric analysis (TGA), Scanning Electron Microscopy (SEM), Energy Dispersive X-Ray Analysis (EDX), X-Ray Diffraction (XRD), and antibacterial tests for two different cultures of bacteria (Staphylococcus aureus and Streptococcus pyogenes). The third method used to obtain thin disks is called compression molding. Following the use of this technology, thin film-type disks were obtained on which experiments such as Oxygen Permeability Test (OTR) and Contact angle measurement were performed. The main conclusions regarding the experimental results obtained for the studied material were as follows:

- the study of the properties was done at the level of coated granules and at the level of the injected sample;
- the studied mechanical properties showed a significant increase of the impact resistance for the parts obtained by injection compared to the injected base material;
- the studied thermal properties were appropriate recommending the material obtained in various applications;
- flexible thin films were obtained by pressing in the mold;
- the antibacterial properties obtained for the injected parts demonstrate that this material can be used in various industries such as the food industry.

There have been many suggestions to conduct production towards modern systems that are more sensitive to environmental issues. For the results to be concrete, the footmark of human actions on ecosystems must be minor than the maximum limit they can withstand before reaching a condition of irreversible degradation. In principle, this result can be obtained through two antithetical orientations: one is based on non-interference, where the set of technological processes are closed on themselves, forming the techno cycles (a principle that is not feasible if not impossible, as in any case for physical reasons there must automatically be an exchange of energy and production of entropy); the other orientation is focused on biocompatibility, which provides for the maximum integration of production with natural processes (biocycle). The goal, in this case, is the realization of systems based on renewable resources reintroduced, at the end of life, into the ecosystem, in the form of totally biodegradable waste. In the footsteps of this orientation, the development of biopolymers has taken on new impetus and vigour over the last few years. These biodegradable materials were already used to produce rubbers such as gutta-percha, caoutchouc, shellac, or even for the production of cellophane. Still, they were “set aside” in favour of resins and synthetic polymers derived from petroleum more advantageous in production, performance, and cost. Nowadays, thanks to the more remarkable manufacturing skills of the industry, biopolymers can be produced much better than the previous ones to the point that it would be possible to use them instead of synthetic plastics. Their dissemination and marketing are greatly influenced by performance and costs. In particular, if attention is focused on performance, the characteristics of the starting raw material impose specific treatments that would weigh on costs. At the same time, they are affected by the low diffusion of such biopolymers on the market and by the price of oil, which affects the production of synthetic plastics and, consequently, on the producer’s choice to orient himself or not towards the biopolymers market. Currently, 99% of plastic materials come from non-renewable resources used both as raw material and as a source of energy within the production process (4% of world oil production becomes plastic). The world currently consumes about 200 million tons of plastic per year (especially in developed countries), with about 25 million tons/year of plastic waste only in Europe and the USA. All this involves not only problems of availability of the raw material for the production of plastics, difficulties linked to the disposal of waste in the post-use phase: in fact, the polyolefins owe their exceptional stability to the long uninterrupted chain of single carbon-carbon bonds, in able to break only over a long period, following oxidation that can be catalysed by natural light. Green composites from renewable resources are increasingly studied because of their potential to benefit the natural environment. Bio-technologies such as Arboblend V2 Nature has several merits into account. Lignin has been blended with several polymers to obtain materials for high added-value applications. This study is set to explore the potential advantages of combining a biopolymer named Arboblend V2 Nature with silver nanoparticles. Silver nanoparticles are known to provide antimicrobial properties for surfaces. Antibacterial activity of silver nanoparticles has been of much interest over the past decade, and silver has been incorporated into different products for antibacterial effect. Surface studies will be carried out on the samples obtained from alloying of Arboblend V2 Nature with silver nanoparticles and the properties of the new material will be determined. Silver plating is one of the earliest electroplating processes. Silver has been conventionally used in the olden days for the aesthetic purpose of improving the appearance of metals. Further, metal finishing has got importance in engineering. It is now extensively used for various applications such as low-end printed-circuit boards (PCB), computer chips, and ICs in the microelectronics industry, self-lubricating coatings used at extreme temperatures in the aerospace industry, etc. Efficient blending is often challenging to achieve, considering the lignin structure's increased complexity and reactivity. The urgent need to replace plastic products with those of biodegradable materials also means a good knowledge of the machinability of these materials through various manufacturing processes. Silver coatings are frequently used to impart antibacterial properties to various surfaces and materials. This application is primarily based on the well-known antimicrobial properties of silver ions (Ag+). It's important to note that while silver coatings can effectively inhibit the growth of microorganisms, their use should be carefully regulated, especially in medical and food-related applications, to ensure the safety of human health and the environment. Additionally, research continues to explore ways to optimize silver coatings for various purposes and mitigate potential risks associated with silver ion release.

Systemic analysis of the injection moulding process

The injection process can be characterized by input and output factors, respectively parameters and disturbing quantities. The optimization of the process can be done by the systematic analysis of the dependencies between the input factors and the output factors, (figure 1-1).

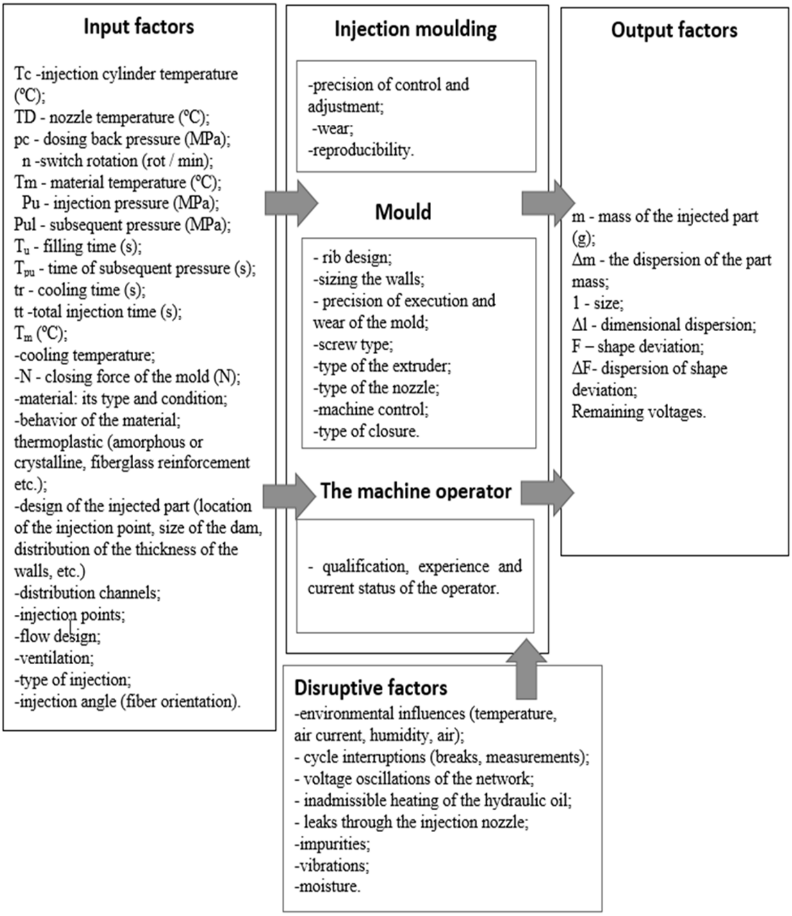


Fig. 1-1. Injection moulding system

The dimensional and weight variation of the injected part is due to the following factors:

- injection machine (precision of control and adjustment, wear, reproducibility);
- behaviour of thermoplastic material (amorphous or crystalline, reinforced with fiberglass, etc.);
- design of the injected part (location of the injection point, size of the dam, distribution of wall thickness, etc.)
- injection conditions (machine adjustment, production run);
- execution and tolerances of the mould.

The contraction and deformation of the injected parts are also influenced by a series of factors presented in figure 1-2.

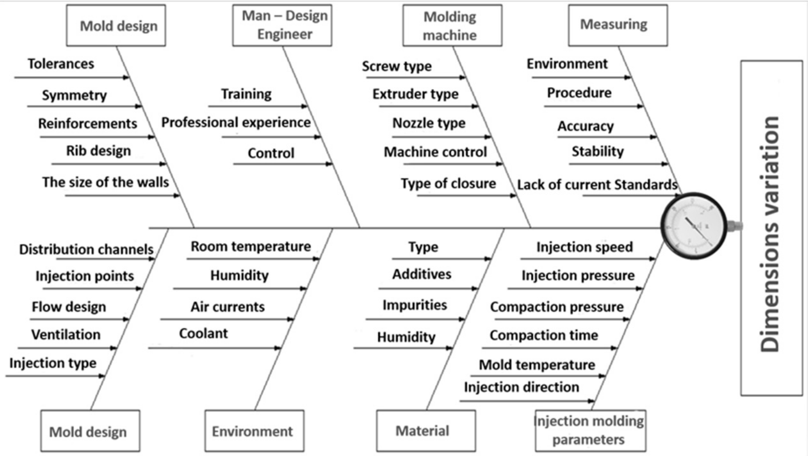


Fig. 1-2. Factors influencing the dimensions and accuracy of parts

The factorial experimental plan

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”.

For the experimental research in this study, three input factors were considered: melting temperature (T_{top}), injection pressure (P_{inj}) and cooling time (t_r). For each factor, two levels of variation were taken into account. So: melting temperature (0 - 155°C; 1 - 165°C) - quantitative factor; injection pressure (0 - 80MPa, 1 - 100MPa) quantitative factor; cooling time (0 - 15s, 1 - 30s), quantitative factor. The three factors, A (melting temperature), B (injection pressure) C (cooling time), each on two levels (0 and 1), generate a factorial experiment 2^3, eight experiments will result ($2^3 = 8$), Table 1-1, as follows:

Table 1-1. 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 equations (1 - 3):

The effect of factor A:

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

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

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

The effect of the interaction of the three factors:

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

or equivalent, equations (4) and (5):

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

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

A graphical representation of the complete three-factor experiment can also be made according to Figure 1-3.

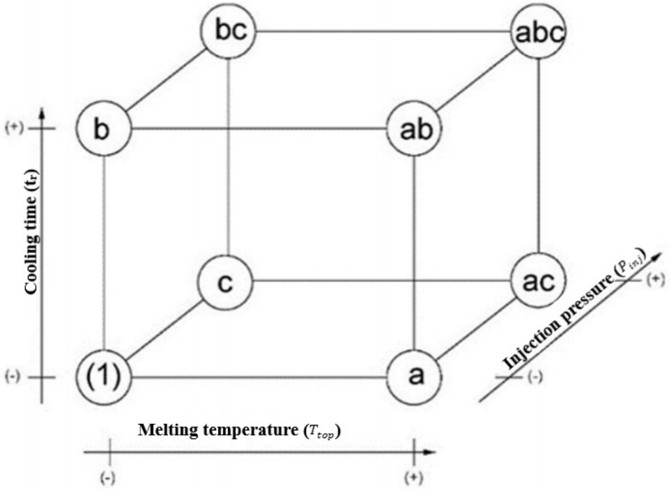


Figure 1-3. Geometrical model of the 2^3 - factorial plan

In this study, 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 study also involved the MiniTab application and went through the following steps, (Yingchoncharoen, Kalinowski and Richardson, 2016, 701-787):

- 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.

The experimental research was carried out according to a complete factorial program of type 2^3 (8 experiments), in which the factors considered were: the melting temperature, injection pressure and the cooling time. The two levels for the three input factors are shown in Table 2.2 which shows the complete factorial plan used for the injection molding of the parts.

Table 1-2. Full experimental plan

Exp. No.	Input parameters		
	T_{top} [°C]	P_{inj} [MPa]	t_r [s]
1	-1(155)	-1 (80)	-1 (15)
2	-1(155)	-1 (80)	+1 (30)
3	-1(155)	+1 (100)	-1 (15)
4	-1(155)	+1 (100)	+1 (30)
5	+1(165)	-1 (80)	-1 (15)
6	+1(165)	-1 (80)	+1 (30)
7	+1(165)	+1 (100)	-1 (15)
8	+1(165)	+1 (100)	+1 (30)

To achieve the experimental (factorial) plan, the ANOVA method will be used in order to quantitatively highlight the effects of the input parameters on the output parameters. According to previous studies in the literature and not only, three input parameters were selected (melting temperature (T_{top}), injection pressure (P_{inj}) and cooling time (t_r)) each with two levels of variation.

2

BIOPOLYMERS: SHORT OVERVIEW

Polymer matrix materials used in technological coating processes

Plastic materials

Polymer engineering is now one of the essential branches of the chemical industry and uses a wide variety of chemicals than any other. The number of commercially essential plastics today is around 50. Application areas for plastics are many and varied; the construction industry, packaging, electronics, recreation, medical, etc. Of the base plastics, 30% are used for packaging, and 20% in the construction industry. There are several ways of classifying polymeric materials. They are massive molecules (polymers) formed by linking up small molecules (monomers) into large chain-like units. If a single type of monomer is involved in developing the polymer, it is called a homopolymer. If two or more different types are concerned, it is called a copolymer. Polymers can also be classified in other ways. If the monomers link up into long chains by joining bonds, and nothing is eliminated in the process, the polymerization is called an addition reaction. If two or more different monomers react with each other, eliminating a simple molecule such as water, this polymerization is called a condensation reaction. The words plastic and resin are often used synonymously. However, strictly, plastics are synthetic macromolecular end products. At the same time, the term resin is used to denote all low, medium, and high molecular weight intermediate synthetic substances from which plastics are made. Natural rubbers and cellulose do not fit into these definitions because their starting material is genuine and not synthetic. For traditional and practical reasons, plastic materials can be divided into three major types: thermoplastic, thermosetting, and elastomers. The thermoplastic resins are characterized by softening when exposed to heat, and when soft, they can be made to flow and assume desired shapes. When cooled, they become hard again. When heated for the first time, the thermosetting resins undergo further chemical reactions in which cross-links develop between polymer chains, holding them rigid in the desired position. They do not soften on reheating like the original polymer. Examples of thermoplastic resins are polyethylene, polystyrene, polyacrylates, polyvinyl chloride, and saturated polyesters. Types of thermosetting resins are: phenol-formaldehyde resins, epoxy resins, and polyurethanes, and elastomers are natural rubbers (Björkner, Bert. 1995, 539-72) Figure 2-1 reveals the classification of the thermoplastic materials.

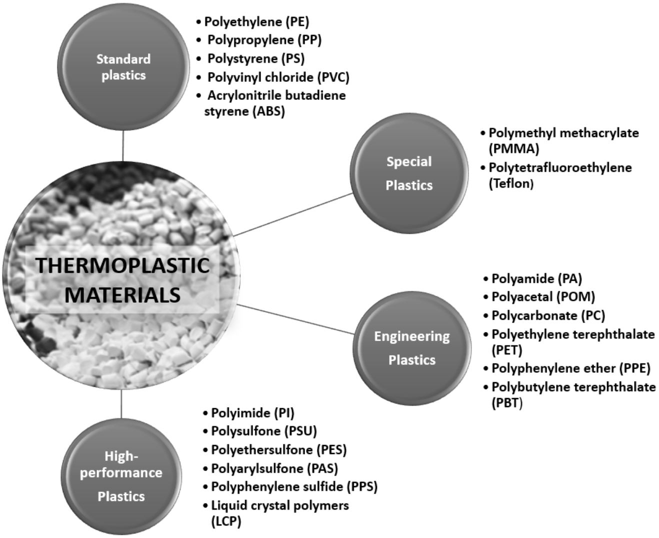


Fig 2-1. Classification of the thermoplastic materials

Biopolymers

At the base of the creation of biopolymers, there is the natural process of photosynthesis: thanks to solar radiation, plants can 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. Bio-polymers are materials obtained from both renewable and non-renewable sources. There are:

- Biopolymers of synthetic origin (from oil sources) and biodegradable;
- Biopolymers from renewable sources (biochemical polymers) that are not biodegradable.

In the latter case, the resulting polymers can be divided into three main categories based on their origin and their production:

- Polymers directly extracted from natural material (mainly plants). This Category includes polysaccharides such as starch and cellulose and proteins such as casein and gluten (I Category).
- Polymers produced by "classic" chemical synthesis using biological and renewable monomers. An excellent example is a polylactic acid, a polymerized bio polyester from lactic acid monomers. The monomers, in turn, can be produced by the fermentation of carbohydrates contained in foodstuffs (II Category).
- Polymers produced by microorganisms or genetically modified bacteria. Essentially, we speak of polyhydroxyalkanoates (III Category).

The problems associated with biopolymers are threefold: performance, processability, and costs. Although these factors are somewhat related, the issues reported to performance and processability are more pronounced with polymers extracted directly from biomass. On the contrary, the polymers belonging to categories two and above, cited above, generally present excellent performances and can be transformed into films using the standard techniques already used for conventional materials. However, these tend to be more expensive when compared to synthetic materials (performance and process alloy).

I Category. They are the most commonly available biopolymers, extracted mainly from plants and animals, both agricultural and marine. Examples are cellulose, starch, pectins and chitins, and proteins such as casein, whey protein, collagen, and soy protein. All these polymers are, by nature, hydrophilic and sometimes crystalline characteristics that cause problems of performance and processability. Cellulose is a great example. Known as the most abundant natural polymer on Earth; and is essentially a non-branched glucose polymer. Thanks to the stable structure and the hydrogen bonds that form between the hydroxyl groups present on the adjacent chains, the cellulose chains aggregate, forming fibrils, which in turn wrap themselves in a spiral forming the fibers. Cellulose is a very economical material but challenging due to its hydrophilic nature, insolubility, and crystalline structure. For the production of cellophane film, the cellulose must be dissolved in a very toxic and aggressive mixture of sodium hydroxide and carbon disulfide with the production of sulfuric acid.

Cellophane has good mechanical properties, but it always remains hydrophilic, is not thermoplastic, and cannot be heat-sealed. Cellophane is often coated with NC-W or PVDC to make up for its poor moisture barrier properties. On the other hand, it has excellent barrier properties against gases, even if these are reduced in the presence of medium and high relative humidity. Alternatively, there is a large number of cellulose derivatives on the market. These are mainly carboxymethyl cellulose, methylcellulose, ethylcellulose, hydroxyethylcellulose, hydroxypropyl cellulose, and cellulose acetate. Of all the results, only the latter is used in food packaging, thanks to the excellent barrier properties. It is well suited to producing plastic films, even if it requires more than 25% plasticizing agents. Indeed, many cellulose derivatives have excellent film-forming properties but are simply too expensive for large-scale use. This is a direct consequence of the crystalline structure of the cellulose that makes the initial derivation process costly and complex. Starch, the polysaccharide of cereals, legumes, and tubers, is another economic raw material, renewable and widely available. This material is biodegradable and inexpensive but also hydrophilic (poor barrier properties against water vapor). It is also partially crystalline and alone cannot form films with good mechanical properties unless treated with plasticizers, bound with other materials (mainly synthetic polymers such as polyvinyl alcohol, although it is still susceptible to moisture) genetically or chemically modified. However, there are few modified starches on the market. Although the starch is less crystalline and more chemically accessible than cellulose, the process remains expensive, and it is necessary to use “light” treatments to avoid starch degradation.

Further progress is needed to develop the full potential of the material. However, it remains the most promising polysaccharide for biofilm production, thanks to its availability, low cost, biodegradability, and the fact that it is more easily processed than cellulose. The challenge is to develop strategies that improve the barrier properties and stability of the films without eliminating these favorable factors. Proteins are used to produce adhesive and edible films but have also been carefully considered for producing packaging films since the coatings made possess excellent gas barrier properties. However, as with starch, the mechanical and barrier properties are affected by relative humidity, again due to the hydrophilic nature of proteins. Also, in this case, the solutions that can be undertaken are the coupling with other materials or the chemical modification. Only keratin is insoluble, but due to its particular structure and the high content of cysteine groups, it is also challenging to process, and the mechanical properties are still scarce (https://www.european-bioplastics.org/ Accessed in 24 of May 2020). Casein, gluten, and soy protein, on the other hand, have good mechanical properties and do not dissolve directly in water but partly absorb it, so they show a specific water resistance, but only under certain conditions. Studies are currently underway on natural proteins derived from whey. The project is called Wheylayer and is funded by the EU. Its main objective is to create a film with a lower decomposition rate (and therefore with a longer useful life than the other BP) by exploiting the excellent barrier properties of whey to oxygen.

II Category. Using the “classic” chemical synthesis for polymer production, it is possible to obtain a broad spectrum of potential bio polyesters. Of all these possibilities, polylactic acid polymers (PLA) have more significant potential for large-scale production and use. Lactic acid, the monomer at the base of polylactic acid (PLA), can be easily obtained from the fermentation of foodstuffs rich in carbohydrates, such as corn or wheat, or waste products from agriculture and industry. Polylactic acid is a polyester whose properties are closely related to the relationship between the two stereoisomers (D and L) of lactic acid.

III Category. Polyhydroxyalkanoates (PHAs), of which polyhydroxybutyrate (PHB) are well-known, are synthesized by some microorganisms and then used as a source of energy and carbon. Some PHAs can also be obtained by fermentation. They are biodegradable and biocompatible, but their properties depend on the monomer composition, which depends on the nature of the carbon source used for the synthesis. In general, they have excellent film-forming, processability properties and are water-resistant. Due to their mechanical and barrier properties look very much like synthetic polymers (PE, PP, PET). Once again, the obstacle to overcome is the cost of production, whose reduction seems much less close than that of the PLA. Lignin-polymer blends depending on the compatibility between lignin and different polymer matrices, the resulting blends can either form miscible blends or display a phase separation. Lignin, a relatively polar polymer due to its numerous structural OH groups, generally presents a high affinity towards polar polymer matrices. Miscible blends were observed in Kraft lignin with polyethylene oxide (PEO) and polyethylene terephthalate (PET) blends, while immiscible blends were found in Kraft lignin with polypropylene and polyvinyl alcohol (PVA) (Kadla and Kubo 2004, 395-400). The compatibility of lignin blends is evaluated by blend morphology, investigated through microscopy, and by assessment of lignin solubility, determined by UV absorbance methods. The major drawbacks of lignin usage as an amorphous thermoplastic component in the formulation of various polymer materials is associated with its relatively high glass-transition temperature and, consequently, by its difficulty to process through thermal blending routes, when lignin undergoes self-condensation reactions through extensive cross-linking and strong intramolecular interactions at high-temperature conditions, leading to inherent brittleness. Normally, these processing issues can be overcome through the blending of lignin with synthetic polymers (including copolymerization approach), biopolymers, through the utilization of plasticizers, or chemical modification techniques. Lignin is effective as an antioxidant and for UV protection due to its radical scavenging ability. Therefore, it is often blended with polymers such as polyethylene, PE, and polypropylene, PP) to improve their thermal-oxidative resistance. Lignin depolymerization is often utilized to improve compatibility with the polymer matrix by decreasing its molecular weight, increasing phenolic content, and reducing aliphatic hydroxyl content. Lignin depolymerization with selective bond cleavage is also performed to minimize lignin condensation, which can often limit the conversion of lignin into value-added products. Chemical modification of lignin is often required to achieve better properties in lignin-polymer blends. In general, lignin, neat or chemically modified, can be used to fulfil the following functions within a blend system: reactive component in the preparation of various resins (e.g. epoxy resins, phenol-formaldehyde resins) and polymers (e.g. 10 polyurethanes), nucleating agent, surfactant, UV blocker, thermal stabilizer, flame retardant, adsorbing agent, reinforcing filler in composites, anti-microbial agent (biocide), supercapacitor for energy storage, carrier (for biomedical and pharmaceutical applications), and precursor for sustainable and cost-effective carbon fibers (Mainka, Tager, Korner, Hilfert, Busse, Edelman nans Herman 2015, 283-96).

Biopolymers and polymers are large molecules composed of repeating subunits but differ in composition, origin, and properties. The differences between biopolymers and polymers are:

In terms of Composition:

- Polymers: Polymers are synthetic or semi-synthetic molecules of various repeating units called monomers. These monomers can be derived from petrochemical sources, such as plastics like polyethylene or polypropylene, or synthesized chemically.
- Biopolymers: Biopolymers are naturally occurring polymers found in living organisms. They are composed of monomers that are typically organic molecules like sugars, amino acids, or nucleotides.

In terms of their Origin:

- Polymers: Polymers can be produced through chemical processes, often involving the polymerization of monomers. They are typically manufactured in industrial settings and can be tailored for specific applications.
- Biopolymers: Biopolymers are produced by living organisms through biological processes. Examples include DNA, RNA, proteins, cellulose, and starch, all essential components of living cells.

In terms of Natural vs. Synthetic:

- Polymers: Polymers can be both natural and synthetic. While some polymers, like cellulose in plants, occur naturally, many polymers are synthesized by humans for various applications, including plastics, adhesives, and coatings.
- Biopolymers: Biopolymers are exclusively natural. They are a fundamental part of biological systems and play essential roles in life processes.

Their Properties:

- Polymers: The properties of synthetic polymers can vary widely depending on their chemical composition and the manufacturing process. They can be designed to have specific mechanical, thermal, and chemical properties for various applications.
- Biopolymers: Biopolymers have unique properties often tailored to perform specific biological functions. For example, proteins are biopolymers that have diverse roles, including enzyme catalysis, structural support, and transport of molecules within cells. DNA is a biopolymer that carries genetic information.

In terms of Environmental Impact:

- Polymers: Many synthetic polymers, especially plastics, can have a negative environmental impact due to their persistence in the environment and contribution to pollution. Efforts are being made to develop more sustainable and biodegradable polymers.
- Biopolymers: Biopolymers are often considered more environmentally friendly because they are derived from renewable resources and can be biodegradable. They can be used in applications where minimizing environmental impact is a priority.

Thus, we can draw the conclusion that polymers incorporate an extensive group of large molecules, both natural and synthetic, while biopolymers specifically refer to naturally occurring polymers found in living organisms. The distinction between the two lies in their origin, composition, and properties, with biopolymers having unique functions within biological systems and often being more environmentally sustainable.

The manufacturing of biopolymers involves the production of polymers that are derived from renewable resources or are decomposable, making them more ecologically friendly than synthetic polymers derived from fossil fuels. Biopolymers can be produced through various methods, including fermentation, chemical synthesis, and extraction from natural sources. The summary of the manufacturing process for biopolymers:

Raw Material Selection:

- Biopolymers are typically derived from natural sources such as plants, bacteria, algae, and animals. Typical raw materials include starch, cellulose, proteins, and various sugars (e.g., glucose, fructose).
- The choice of raw material depends on the desired biopolymer and its intended applications.

In terms of Fermentation:

- Many biopolymers are produced through microbial fermentation. Microorganisms, such as bacteria or yeast, are cultured in bioreactors with the selected raw material as their nutrient source.
- During fermentation, microorganisms metabolize the raw material and produce biopolymers as a byproduct.
- The settings within the bioreactor, counting the parameters such as oxygen level, PH, and temperature, are cautiously measured to improve polymer manufacture.

In terms of Extraction and Purification:

- After fermentation, the biopolymer needs to be extracted and purified. The extraction process varies depending on the type of biopolymer.
- Standard extraction methods include solvent extraction, centrifugation, filtration, and precipitation.
- Purification involves removing impurities and contaminants to obtain a high-purity biopolymer.

In terms Chemical Modification (Optional):

- In some cases, the extracted biopolymer may undergo chemical modifications to enhance its properties or tailor it for specific applications. These modifications can include cross-linking, grafting, or blending with other polymers.

In terms of Processing and Formulation:

- Biopolymers can be processed into various forms, such as films, fibers, sheets, or molded products.
- The processing methods can include extrusion, injection molding, compression molding, and more.
- Additives, plasticizers, and other compounds may be added to improve the properties of the biopolymer and meet specific requirements.

In terms of Quality assurance and control:

- Quality assurance and control procedures are executed during the engineering method to confirm that the biopolymer meets desired specifications and standards.

In terms of Packaging and Distribution:

- The finished biopolymer products are packaged and prepared for distribution to end-users or manufacturers of various products, such as packaging materials, disposable tableware, medical devices, and more.

In terms of Environmental Considerations:

- One of the primary advantages of biopolymers is their biodegradability and reduced environmental impact. Biodegradable biopolymers break down naturally in the environment, reducing waste and pollution.

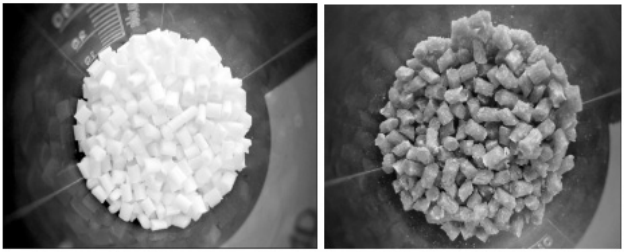
The specific manufacturing process for biopolymers can vary significantly depending on the type of biopolymer being produced and its intended applications. It’s essential to consider factors such as raw material availability, production scalability, and cost-effectiveness when choosing a manufacturing method for biopolymers. Additionally, research and development in the field of biopolymers continue to advance, leading to the development of new and innovative production methods.

Several biopolymers can be considered when it comes to mold casting, especially for applications where you need materials with good moldability and specific properties. The best biopolymer for mold casting will depend on the desired end-use properties, biodegradability, and cost considerations. When selecting a biopolymer for mold casting, the mechanical properties and biodegradability should be considered. Additionally, consider cost, availability, and the intended use of the casted objects. Experimentation and testing may be necessary to determine the best biopolymer for your own application.

Lignin-based polymer materials

Arboblend V2 Nature and other types of liquid wood

Liquid wood is obtained 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® (Figure 2-2).



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

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

Fig 2-2. Different types of liquid wood

Arboblend V2 Nature

According to the manufacturer (http://www.tecnaro.de/en/arboblend-arbofillarboform/ Accessed on 15 December 2019), 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 also 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 individual customer’s needs and the purpose of using the material. This product is also completely recyclable and has the appearance of light wood.

3

NANOPARTICLES: SHORT OVERVIEW

Nanotechnologies characterize engineering on a very small scale. Nanotechnologies manage materials with dimensions in the nanometer scale, approximately between 1 and 100 nm (Laurent et al. 2008). They can be applied in many fields, such as health and medicine, information and communication technology, energy and the environment and not only. Nanotechnologies work at the nanoscale (the scale of individual molecules). Nanotechnology has become more popular in the last decades, and thanks to this technology has been already manufactured several types of materials at a nanoscale level. Physicist and Nobel laureate Richard Feynman is considered the father of nanotechnology since he presented his lecture in 1959.

Nanoparticles are generally separated into several types reliant on their morphology, dimensions and biochemical properties, (Figure 3-1).

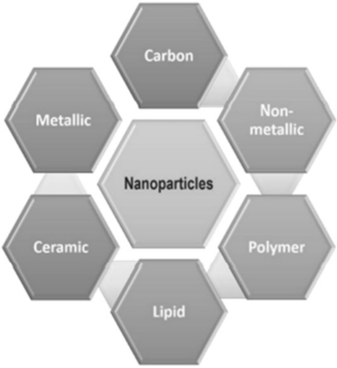


Fig 3-1. Classification of the nanoparticles

Carbon-based nanoparticles

The carbon-based nanoparticles are manufactured entirely of carbon (Bhaviripudi et al. 2007). They can be grouped into fullerenes, graphene, carbon nano tubes (CNT), carbon nanofibers and carbon black and sometimes activated carbon in nano size and are presented in Figure 3-2.

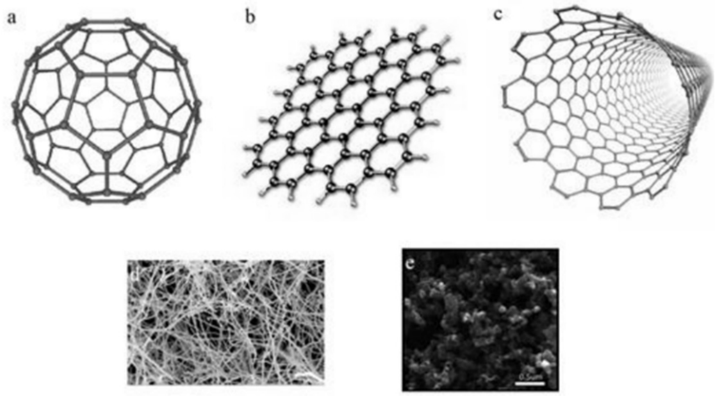


Fig 3-2. Carbon based nanoparticles: a – fullerenes, b – graphene, c – carbon nanotubes, d – carbon nanofibers and e – carbon black (Anu Mary Ealia and Saravanakumar 2017)

Fullerenes (C_{60}) is a carbon molecule that is spherical in shape and made up of carbon atoms held together by sp^2 hybridization. About 28 to 1500 carbon atoms forms the spherical structure with diameters up to 8.2 nm for a single layer and 4 to 36 nm for multi-layered fullerenes.

Graphene is an allotrope of carbon. Graphene is a hexagonal network of honeycomb lattices made up of carbon atoms on a two-dimensional planar surface. Mostly, the thickness of the graphene sheet is around 1 nm.

Carbon Nano Tubes (CNT), a graphene nanofilm with a honeycomb lattice of carbon atoms is wound into hollow cylinders to form nanotubes of diameters as low as 0.7 nm for a single layered and 100 nm for multi-layered CNT and length varying from a few micrometres to several millimetres. The ends can either be hollow or closed by a half fullerene molecule.

Carbon Nanofiber. The same graphene nanofilms are used to produce carbon nanofiber as CNT but wound into a cone or cup shape instead of a regular cylindrical tube.

Carbon black. An amorphous material made up of carbon, generally spherical in shape with diameters from 20 to 70 nm. The interaction between the particles is so high that they bound in aggregates and around 500 nm agglomerates are formed.

Metal and metal oxide-based nanoparticles

Inorganic nanoparticles are particles that are not made up of carbon. Metal and metal oxide-based nanoparticles are generally categorised as inorganic nanoparticles.

Metal based. Nanoparticles that are synthesised from metals to nanometric sizes either by destructive or constructive methods are metal based nanoparticles. Almost all the metals can be synthesised into their nanoparticles (Salavati-Niasari, Davar, and Mir 2008). The commonly used metals for nanoparticle synthesis are aluminium (Al), cadmium (Cd), cobalt (Co), copper (Cu), gold (Au), iron (Fe), lead (Pb), silver (Ag) and zinc (Zn). The nanoparticles have distinctive properties such sizes as low as 10 to 100nm, surface characteristics like high surface area to volume ratio, pore size, surface charge and surface charge density, crystalline and amorphous structures, shapes like spherical and cylindrical and colour, reactivity and sensitivity to environmental factors such as air, moisture, heat and sunlight etc.

Metal oxides based. The metal oxide-based nanoparticles are synthesised to modify the properties of their respective metal-based nanoparticles, for example nanoparticles of iron (Fe) instantly oxidises to iron oxide (Fe_2O_3) in the presence of oxygen at room temperature that increases its reactivity compared to iron nanoparticles. Metal oxide nanoparticles are synthesised mainly due to their increased reactivity and efficiency (Tai et al. 2007). The commonly synthesised are Aluminium oxide (Al_2O_3), Cerium oxide (CeO_2), Iron oxide (Fe_2O_3), Magnetite (Fe_3O_4), Silicon dioxide (SiO_2), Titanium oxide (TiO_2), Zinc oxide (ZnO). These nanoparticles have possessed an exceptional property when compared to their metal counterparts.

Lipid-based nanoparticles

Lipid-based nanoparticles (LBNPs) such as liposomes, solid lipid nanoparticles (SLN) and nanostructured lipid carriers (NLC) have received great attention in drug discovery and cancer treatment. These nanoparticles can transport hydrophobic and hydrophilic molecules, display very low or no toxicity, and increase the time of drug action by means of a prolonged half-life and a controlled release of the drug (Ozpolat, Sood, and Lopez-Berestein 2014).

Liposomes are the most studied delivery systems due to the biocompatibility and biodegradability that they present. The main components of these nanoparticles are phospholipids, which are organized in a bilayer structure due to their amphipathic properties. In presence of water, they form vesicles, improving the solubility and stability of anticancer drugs once they are loaded into their structure. They are capable of encapsulating either hydrophobic or hydrophilic drugs (Yingchoncharoen, Kalinowski and Richardson, 2016, 701-787).

Solid lipid nanoparticles (SLN) represent a relatively new colloidal drug delivery system, composed of physiological lipids that remain in a solid state at both room and body temperature. These particles are in the size range of 50–1000 nm. The solid lipid used forms a matrix material for drug encapsulation and include mono-, di- or triglycerides, fatty acids and complex glyceride mixtures. This matrix is stabilized by a mixture of surfactants or polymers. SLNs have significant advantages, such as site-specific targeting, physical stability over a long period, possibility of controlled release of both lipophilic and hydrophilic drugs, protection of labile drugs, low cost, ease of preparation and nontoxic. Furthermore, in reference to toxicity, SLNs have exceptionally low toxicity effects against human granulocytes. All these outstanding advantages make them an important candidate for drug delivery systems (Rabiatul Basria S. M. N. Mydin and Said Moshawih 2018).

Nanostructured lipid carriers (NLC) represent a second generation of lipid-based nanocarriers, developed from SLN, which comprise a combination of solid and liquid lipids. This system was developed in order to overcome the limitations of SLNs; hence, NLCs have higher drug loading capacity, and could also avoid drug expulsion during storage by avoiding lipid crystallization due to the presence of liquid lipids in the NLC formulation. While SLNs are composed of solid lipids, NLCs are a mixture of solid and liquid lipids, such as glyceryl tricaprylate, ethyl oleate, isopropyl myristate and glyceryl dioleate. The mean particle sizes are highly similar to SLNs, generally in the range of 10–1000 nm, and are affected by the nature of the containing lipids and the manufacturing process. The main advantages of these nanoparticles are that they can be loaded with hydrophilic and hydrophobic drugs, can be surface-modified, lend themselves to site-