Bio-based multilayer films: A review of the principal methods of production and challenges

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Abstract

The development of biodegradable packaging materials has been drawing attention worldwide to minimize the environmental impact of traditional petroleum-based plastics. Nevertheless, it is challenging to obtain bio-based materials with suitable properties for packaging applications. Films produced from a single biopolymer often lack some important properties. An alternative to overcome this limitation is the multilayer assembly. Under this technology, two or more materials with specific and complementary properties are combined into a single-layered structure, thus improving the performance of bio-polymer plastics.

This review presents the main aspects of bio-based multilayer film production technologies, discussing their advantages and disadvantages, which have to be considered to produce the most suitable film for each specific application.

Most of the studies reported that such films resulted in increased mechanical performance and decreased water, oxygen, and dioxide carbon permeability. This approach allows the addition of compounds leading to antioxidant or antibacterial activity. Finally, a discussion about the future challenges is also presented.

Keywords: biodegradable, packaging, plastic, biopolymers, casting, extrusion, moulding, electrospinning, Layer-by-Layer deposition

Abbreviations

CH	Chitosan
GEL	Gelatin
LbL	Layer-by-layer
PCL	Polycaprolactone
PBS	Poly (butylene succinate)
LDPE	Low-density polyethylene
PEG	Poly (ethylene glycol)
PHA	Polyhydroxyalkanoates
PHBV	Poly(3-hydroxybutyrate-co-3-valerate)
PI	Protein isolate
PLA	Polylactic acid
PVA	Poly (vinyl alcohol)
S	Starch
WG	Wheat Gluten
Z	Zein

1. Introduction and contextualization

In the last decades, the search for replacing petroleum-based plastics with biobased ones has led to a great number of studies using biodegradable polymers. With regard to an environmentally friendly claim, most of the studies aimed to obtain plastics with comparable performance to those of plastics made from petrochemical polymers.

The interest in these plastics arises primarily from their originating from renewable raw materials (crops instead of crude oil). However, it is well known that films made from a single biopolymer rarely have a competitive edge against synthetic films, limiting their applications (Bora and Mishra 2016). For instance, starch-based films and gelatin-based films generally present high hydrophilicity and water permeability (Muller et al., 2017a; Nilsuwan K, & Benjakul S, 2018). Hence, some alternatives were proposed to overcome these limitations.

An alternative is modifying the natural biopolymers to improve their properties. For instance, considering starch, different modification techniques, such as ozonation, ultrasound, pulsed electric fields, microwave, dry heating temperature have been employed to improve the processability, mechanical and/or barrier properties. However, although interesting results were yielded and some properties improved, such as the mechanical, other properties were decreased like the barrier ones (La Fuente et al. 2019; 2020).

Polymer blending is another well-used strategy to improve film properties; positive results were discussed in some studies in the literature (Fonseca-García, Jiménez-Regalado, and Aguirre-Loredo 2021; Barizão et al. 2020; Ochoa-Yepes et al. 2019). However, some challenges need to be overcome to form a blend, such as reducing the interfacial tension and improving adhesion between the two polymers (Vuksanović and Heinemann 2019)

Another interesting strategy is to combine several layers, each one with particular properties, into multilayer assembly results in materials with improved characteristics (Vartiainen J et al. 2015). Currently, petrochemical-based materials are already used to produce multilayer association. In most commercial applications, multilayer films consist of a number of layers of different polymers, ranging from 3 to 12 layers ("Polymer Properties Database" 2020).

Concerning the bio-based multilayer films, interesting results have been achieved by adopting the multilayer approach, such as improving the mechanical and barrier properties (Muller, González-Martínez, and Chiralt 2017a; Requena, Vargas, and Chiralt 2018; Andrade-Del Olmo et al. 2019; Balik et al. 2019). Some layers are used to provide mechanical resistance, while others act as gas and moisture barriers (Tampau et al., 2020). Generally, the outer layers provide good water barrier and mechanical properties and the inner layers provide a good gas barrier (Kurek et al. 2012). Moreover, antimicrobial or antioxidant molecules can be added to the multilayer structures, leading to additional benefits as an active packaging (Tampau et al., 2020). This multilayer approach has a huge potential to produce films with optimal properties. Nevertheless, further studies on the effects of different combinations of layers and polymers and the way they are produced still need to be further investigated.

Therefore, in this study, we review and discuss the bio-based multilayer films obtained in the last years. The main production technologies are presented and discussed, as well as future challenges and perspectives.

2. Biopolymers

Biopolymers are substances composed of many subunits obtained entirely from renewable resources, which could be directly obtained from the biomass, by chemical synthesis or produced by microorganism (Shafqat et al., 2020). A bio-based plastic is obtained from a biopolymer, such as polysaccharides, proteins, among others (Polska, 2019).

A bio-based plastic can naturally degrade, but the conditions in which this takes place will define if they can be considered "biodegradable" or "compostable", according to local standards (UNEP, 2015). However, sometimes these terms (biodegradable and compostable) can cause some misunderstanding and will be briefly described as follows.

By definition, biodegradable plastics are those decomposed by the action of living organisms (Wierckx et al. 2019). A biodegradable plastic could be a bio-based or petroleum-based plastic, the latter, with additives to enhance its biodegradability (UNEP 2015). The biodegradation process depends on the conditions (e.g. location, temperature, humidity, presence of microorganisms, etc.) of the specific environment (industrial composting plant, garden compost, soil, water, etc.); consequently, this process of degradation can fluctuate significantly (European bioplastics 2016). Sometimes biodegradable materials leave behind a residue named microplastic, which are tiny plastic particles (up to 5 mm in diameter) (UNEP 2013; Wei et al. 2021) when returning to nature, they can accumulate in the ocean and soils and pose a significant risk to ecosystems all over the world (UNEP 2013; Wei et al. 2021). Contrary to the expected, a microplastic is not only produced from a petroleum byproduct, but also from bio-based polymers (Wei et al. 2021). For example PLA produce a large number of microplastics during biodegradation and have a very long lifetime (Wei et al. 2021).

In turn, compostable materials are also biodegradable under specific conditions (e.g. a certain temperature, timeframe, etc) and create humus, which is full of nutrients and a great fertiliser for plants (Enviroment 2020). The specific conditions of degradation (biodegradability and/or compostability) are described in local standards, such as for industrial composting (EN 13432, ASTM D6400); in marine environment (ASTM

D6691, ISO 18830, ISO 19679), in soil (EN 17033), in home composting (AS 5810), among others (Greene 2014; European Environment Agency 2020; European bioplastics 2016). Materials and products complying with these standard can be certified and labelled accordingly (European bioplastics 2016).

Different researchers have studied the production of bio-based plastics. For exemplifying, the currently most relevant biopolymers applied to the production of films, starch, chitosan, zein, gelatin and polylactic acid, were selected and described as follows.

2.1.Starches

Starch is a carbohydrate formed mainly by two polymers: amylose and amylopectin. It is considered one of the best biopolymers for packaging applications, with great potential and interesting characteristics, such as biodegradability, availability in huge quantities, and low cost. Moreover, this biodegradable and non-toxic biopolymer is able to form gels and pastes with a sufficient amount of water and heating. Starch is already broadly employed as an industrial ingredient, with applications in different areas, such as food, paper, textile and chemical (Maniglia et al. 2020).

Starch can be obtained from various sources, such as cereals, roots, tubers and grains, the main sources of commercial starches being corn, wheat, cassava, potato and rice. Each starch source presents distinct features, such as granule size and morphology, molecular weight, amylose/amylopectin ratio and length, as well as characteristic properties, such as the temperature of gelatinization, the pasting capacity and gel strength, among others (Ojogbo, Ogunsona, and Mekonnen 2020; Vu and Lumdubwong 2020; Maniglia et al. 2020).

Unfortunately, starches in their native form present limited functionalities, which can hinder their applications to material engineering (Maniglia et al. 2020). In films production, some disadvantages of using starch include its limited water dissolvability at room temperature, strong hydrophilic behavior, low thermal stability, and films with high rigidity, permeability to water vapor and poor mechanical properties (Shafqat et al. 2020; de Oliveira et al. 2020; Fonseca-García, Jiménez-Regalado, and Aguirre-Loredo 2021; Ojogbo, Ogunsona, and Mekonnen 2020).

Different strategies have been studied and employed to improve the quality and functionality of starch-based films. For example, the addition of reinforcement filler, such as cellulosic materials and the combination of starch with other polymers, producing copolymers and blends (Tavares et al. 2020; Soni et al. 2020; Menzel 2020; de Oliveira et al. 2020); i.e. the addition of κ-carrageenan has no significant effect on water vapor permeability, but increases tensile strength and Young's modulus of cassava starch-based films (Barizão et al. 2020). Similarly, films are made from cassava starch blended with lentil proteins produced by casting and extrusion (Ochoa-Yepes et al. 2019). In fact, the methods of production, challenges and future perspectives of starch-based plastics is reported in some studies (Abdullah & Dong, 2018; Siqueira et al., 2020; Su & Cheng, 2011).

Another strategy is related to starch modification. Several characteristics can be changed and functionalities can be improved by modification processes. For this, different methods, including chemical, physical, enzymatic, and genetic, can be used to obtain starches with suitable properties for each type of application. Particularly, there has been an increasing interest to develop sustainable or “green” methods for starch modification, such as ozone and plasma treatment (chemical modification) and heat moisture treatment (thermal modification) (Maniglia et al. 2020; Ojogbo, Ogunsona, and Mekonnen 2020).

Starch modification by cold plasma is mainly based on crosslinking and depolymerization mechanisms. For example, in films made from plasma-modified corn starch, lower water vapor permeability was achieved when compared with native starch-based films (Sifuentes-Nieves et al. 2020). Besides, plasma modification allowed to either increase or decrease the rigidity of films, as revealed by the tensile strength and elongation at break values, depending on the starch amylose content (Sifuentes-Nieves et al. 2020).

Ozonation increases the carboxyl and carbonyl contents and reduces the molecular size of starch (Castanha, Matta Junior, and Augusto 2017). The ozonation of cassava starch resulted in films with improved strength and better mechanical properties (higher tensile strength and Young's modulus) (La Fuente et al. 2019). However, lower barrier properties were also observed, as revealed by higher water vapor and oxygen permeabilities (La Fuente et al. 2019; 2020).

2.2. Chitosan

Chitosan is a natural linear amino polysaccharide and a unique polycationic polymer. It is mainly obtained from the partial deacetylation of chitin (Priyadarshi and Rhim 2020; Elsabee and Abdou 2013). Chitin is the second-most abundant polysaccharide present in nature after cellulose and it is the main component of the exoskeleton of arthropods, being the most abundant biopolymer of animal origin. Chitin can be obtained from marine crustaceans, especially crabs, lobsters, and shrimps, and also from terrestrial arthropods, including insects and arachnids (Haghighi et al. 2020). In general, crustacean shells, such as those from crabs and shrimps, are the main sources of chitin for industrial and commerical use due to the availability of wastes from the sea food processing industries (Kaur and Dhillon 2015). Chitosan can also be extracted directly from some fungal sources (Priyadarshi and Rhim 2020).

Chitosan presents several interesting characteristics, including biocompatibility, biodegradability, versatility, antimicrobial activity against various microorganisms, antioxidant activity and film-forming nature (Shin et al. 2002; Shapi'i et al. 2020; Nair et al. 2020; Fonseca-García, Jiménez-Regalado, and Aguirre-Loredo 2021; Kumar, Mukherjee, and Dutta 2020). Chitosan-based films have shown to be very good barriers to the permeation of gases, such as oxygen (Shin et al. 2002; Fonseca-García, Jiménez-Regalado, and Aguirre-Loredo 2021; Martínez-Camacho et al. 2010). Thus, chitosan has been widely used in food preservation and packaging applications (Bharathi et al. 2020; Liu et al. 2020).

Nevertheless, chitosan presents low solubility in water and in various organic solvents, which impairs a broader application of these biopolymers. In general, their solubility can be favored in acidic media (pH<6) and a high degree of deacetylation. In fact, the degree of deacetylation is a very important chemical characteristic of chitosan, which represents the content of N-acetyl-glucosamine and D-glucosamine copolymer that is formed by the partial replacement of acetyl groups (Kumar, Mukherjee, and Dutta 2020). Therefore, this information is necessary for the specification and classification of chitosan. In fact, the degree of deacetylation influences not only the solubility of chitosan, but also the rheology of the film-forming solution and the antimicrobial activity (Priyadarshi and Rhim 2020; Van Den Broek et al. 2015).

However, some limitations of films made with chitosan are related to low water resistance and susceptibility to ultraviolet degradation, which limits their use (Haghighi et al. 2019; Nair et al. 2020; Van Den Broek et al. 2015). Therefore, in order to improve chitosan-based film properties and functionality as a food packaging material, the incorporation of nanofillers, such as cellulose nanofibers, silver nanoparticles and nano-silica, and the blending of chitosan with other polymers are examples of approaches that have been studied (Zhang et al. 2020; Haghighi et al. 2020).

Chitosan can be blended with various biodegradable polymers, including polysaccharides and proteins. Generally, films formulated with chitosan and polysaccharide blends show advantages when compared to films made from proteins and lipid blends (Nair et al. 2020). Chitosan/polysaccharides-based films are relatively stable and present good heat sealability and water solubility (Li et al. 2019). Particularly, blends of chitosan and alginate present excellent biocompatibility by forming a polyelectrolyte complex. Their films present good barrier properties against lipids and gases (Nair et al. 2020; Priyadarshi and Rhim 2020). However, when directly blending chitosan and alginate, the mixture can form a highly viscous gel, making it difficult to degas. Therefore, different methods can be employed for preparing films to overcome this potential issue, as layer-by-layer (LbL) assembly (Li et al. 2019), which will be further discussed in the next sections.

Blends of chitosan and starches from different sources have been largely studied. In general, blending chitosan and starch, especially starch with a high content of amylose, results in the formation of strong hydrogen bonds between these polymers and, thus, films with high stability in comparison to their respective monolayers (Nair et al. 2020). In general, the combination with chitosan allows an improvement of the mechanical and water barrier properties of starch-based films (Kumar, Mukherjee, and Dutta 2020). In corn starch-chitosan blended films, while the inclusion of chitosan (with an 88% degree of deacetylation) gives rise to an increase in tensile strength and elongation at break, a decrease occurs in Young's modulus and water vapor permeability in comparison to the neat starch matrix (Ren et al. 2017). In wheat starch-chitosan blended films, the addition of chitosan (degree of deacetylation >77%) improved tensile strength and elastic modulus, but slightly affected the oxygen and water vapor permeability (Bonilla et al. 2013). Fonseca-García et al. (2021) evaluated the values of solubility in water at room temperature and observed a solubility of 21% and 76% for the starch and chitosan (deacetylation degree ≥75%), respectively, while mixing both polymers, the resulting film had an intermediate solubility of 42%. An analogous finding was observed when evaluating water vapor permeability.

2.3.Proteins

Proteins are interesting biopolymers because they are able to form a cohesive and continuous matrix and present functionality related to selective binding and mechanical strength (Ojogbo, Ogunsona, and Mekonnen 2020). In general, protein-based films generally have better gas barrier and mechanical properties compared to polysaccharide films. Several protein sources have been explored for material applications, including plant, animal and fungi sources. Various types of protein have been studied, such as gelatin, casein, whey, zein, wheat gluten and soy proteins (Coltelli et al. 2016). Among these, zein (example of globular protein) and gelatin (example of fibrous protein) have been selected to be further described, since they are extensively applied to develop biodegradable films.

Zein, the prolamine of corn, has attracted industrial and research interest, especially for food wrapping purposes. Zein presents interesting features, including plasticity, biodegradability and heat seal property (Mensitieri et al. 2011). In addition, zein presents a particular hydrophobicity due to its high content of nonpolar amino acids, such as leucine, alanine, and proline. Zein is thus insoluble in water but soluble in alcoholic solutions (Nogueira and Martins 2019). Generally, zein-based films offer better moisture barrier properties than other proteins, such as casein, or polysaccharides, as starch (Mensitieri et al. 2011). Besides, zein-based films present great stability in high humidity and heat. Nevertheless, zein films show poor mechanical properties and high solubility when compared to other proteins, such as gluten and fish protein (Nogueira and Martins 2019). The incorporation of chitosan nanoparticles to the zein-based films improves their thermal stability and tensile strength; however, it reduces their values of elongation at break and increases the brittleness of the films (Cui et al. 2020).

Gelatin is a water-soluble protein derived from the partial hydrolysis of collagen, which is the main constituent of animal skin, bone, and connective tissue (Chuaynukul et al. 2018). Commercially, bovine and porcine skin and bone are usually the sources of gelatin production, although fish gelatin has been gaining attention recently (Chuaynukul et al. 2018; Nilsuwan, Benjakul, and Prodpran 2018; Nogueira and Martins 2019). Gelatin has been widely used as a material for biodegradable film formation since it has an excellent film-forming ability. Gelatin-based films have good gas barrier properties and relatively good mechanical properties, but poor barrier properties against water vapor (Chuaynukul et al. 2018) due to the hydrophilic nature of gelatin (Nilsuwan, Benjakul, and Prodpran 2018).

As a consequence, different polymer blends have been proposed to improve the functionality of gelatin-based films. For example, when gelatin is blended with chitosan; the resulting gelatin-chitosan blend films show improved moisture barrier and higher tensile strength than the respective monolayers. The blend of gelatin and chitosan presents good compatibility, as verified by the electrostatic interactions and hydrogen bond formation (Haghighi et al. 2019). Similarly, blending gelatin with starch may also enhance film properties. Blending gelatin with tapioca starch improves the water-resistance of the films and increases the thermal stability, tensile strength and elongation at break values. In the case of gelatin-potato starch blended films, the addition of starch increases water vapor permeability and impairs the mechanical properties (Podshivalov et al. 2017). In particular, this finding further highlights the importance of film characterization to observe the effects of components of the blends on properties of the film.

2.4. Polylactic Acid

Polylactic acid (PLA) is a linear aliphatic thermoplastic polyester, obtained from lactic acid monomers produced from the fermentation of renewable and biodegradable plant sources, such as corn or rice starches and sugar feedstocks (Muller, González-Martínez, and Chiralt 2017b). PLA is a very promising biodegradable polymer, since it shows versatility, excellent processability, reasonable mechanical properties, high transparency, and relatively low cost as well (Cherpinski et al., 2018; Nilsuwan et al., 2018). Some properties of PLA, such as degree of crystallinity, melting and glass transition temperatures, can be tailored by controlling the monomer composition of the two optical isomeric forms (Mensitieri et al. 2011).

Despite these several positive characteristics, PLA also presents downsides, such as poor heat sealing capacity and relatively low oxygen barrier properties (Mensitieri et al. 2011). Therefore, as with other polymers, the strategy of making blends to improve the material functionality has also been extensively studied with PLA. However, since PLA is hydrophobic, its compatibility is affected when mixed with hydrophilic biopolymers, such as starch (Muller, González-Martínez, and Chiralt 2017b). To overcome this limitation, different strategies have been evaluated, including polymer modification and addition of compatibilizers to the blends, such as methylenediphenyl diisocyanate, maleic anhydride and poly(ε-caprolactone) to improve the miscibility (Bie et al. 2013).

3. Multilayer associations

Multilayer films of traditional plastics are widely applied in the high-volume packaging industry ("Polymer Properties Database" 2020). The key factor for multilayers assembly is the bonding between layers. The main mechanisms to produce adhesion include mechanical interlocking, diffusion, electron transfer, and adsorption (Vartiainen et al., 2015). However, migration of species such as plasticizers, from one layer to another, can be a major drawback in multilayer films (Kurek et al. 2012). Physical surface activation treatments are used to enhance the wettability of surfaces and to increase the interlayer bonding (Vartiainen et al., 2015).

Currently, multilayer films are successfully produced by different methods e.g. casting, compressing moulding, extrusion, layer-by-layer (LbL) deposition and electrospinning. A schematic representation of these main methods is presented in Figure 1.

The number of studies published according to the Web of Science database for each production process considering de period from 2016 to 2020 is shown in Figure 2. The terms used in the research were: TS=((film) AND (*bilayer* OR *multilayer*)) AND AB=(LbL AND (bilayer OR multilayer) AND film) for LbL; TS=((film) AND (*bilayer* OR *multilayer*)) AND AB=(cast* AND (bilayer OR multilayer) AND film) for casting; TS=((film) AND (*bilayer* OR *multilayer*)) AND AB=(mo$ld* AND (bilayer O R multilayer) AND film) for compression moulding; TS=((film) AND (*bilayer* OR *multilayer*)) AND AB=(extrusion AND (bilayer OR multilayer) AND film) for extrusion; TS=((film) AND (*bilayer* OR *multilayer*)) AND AB=(electrospinning AND (bilayer OR multilayer) AND film) for electrospinning.

As shown in Figure 2A, > 50 % of the studies were published using the LbL technique, followed by the casting process. The main advantages of the LbL technique is its simplicity, low cost, and versatility in manufacturing processes using different types of materials (Gezgin et al., 2017; Pinto et al., 2017). Moreover, the film growth rate can be well controlled at the nanometer scale, which is commonly a linear function of the number of the layer pairs deposited (Michel et al. 2012).

Although casting technique is the second technique when considering the number of publications (Figure 2A), studies involving compression moulding, electrospinning or extrusion were higher than those involving casting in the last two years, probably due to the challenges involved to scale-up this type of process.

Most of the studies involve the combination of one or two technologies e.g. casting-compression moulding; casting-electrospinning; casting- LbL, etc. A few studies involve the combination of more than three technologies, such as the one by Rocca-Smith et al. (2019), producing a PLA-Wheat gluten-PLA tri-layer association. In the next section, each production process and the main combinations are explored.

4. Production process

4.1.Layer-by-layer deposition

The Langmuir-Blodgett deposition, or most commonly named layer-by-layer deposition method, consists of transferring amphiphilic molecules from the water-air interface to a solid-air interface (Michel et al. 2012). The main advantages are low cost, simplicity, and versatility in manufacturing processes of highly ordered multilayer film using various types of materials (Gezgin et al., 2017; Pinto et al., 2017). However, it is a time-consuming process and also produces chemical waste, which generally limits industrial applications (Akagi, Fujiwara, and Akashi 2012).

There are only two basic requirements for LbL deposition: the polyelectrolytes of interest must be water-soluble and they must carry an opposite electrostatic charge (Gezgin, Lee, and Huang 2017). LbL deposition could be applied by three alternatives: dip-coating, spray-coating and spin-coating. The first one is a well-established method and the most commonly used. Table 1 summarizes representative studies using this technology, which consists in the sequential adsorption of alternating monolayers of two components by attractive forces (Pinto et al. 2017).

In turn, in the spray LbL deposition, the first layer surface is coated with aerosolized droplets of the polyelectrolyte solution, instead of submerging (Nogueira et al., 2011). The advantages are the ability to coat large irregular pieces uniformly and the significantly reduced time (>90%). Furthermore, the spray method generates less waste, which is both cost-effective and beneficial for the environment (Denis-Rohr A, Bastarrachea LJ 2015). Chitin nanofibers and cellulose nanocrystals were spray coated directly onto a PLA film. Reductions were observed in O_2 permeability relative to neat PLA, even at elevated RH (70%) (Satam et al. 2018). Criado-Gonzales et al. (2019) produced a multilayer film with Alginate and chitosan through spray-coating and a specific drug against breast cancer was incorporated. It was observed that this multilayer could be employed for sustained drug delivery and that its therapeutic effect can be optimized by the number of bilayers.

Combinating casting with LbL is also possible; Dai et al. (2017) produced the first layer by casting using a solution of 0.5 wt % of cationic guar gum. Then, anionic cellulose nanofibrils and cationic guar gum were LbL deposited onto the first monolayer. The resulting multilayer films were transparent, strong and exhibited good gas (water vapor and oxygen) and oil barrier performances in comparison to the cationic guar gum monolayer. De Andrade et al. (2017) formed a monolayer cast film with Polyhydroxyalkanoates **(**PHA) through a solution of 8 g of PHA at 8 in 60 mL of $CHCl_3$. This film was dip-coated with a filmogenic solution prepared with two macromolecules, gelatin (GEL), cheese whey (CW) and glycerol, forming a total of three layers (pure PHA wrapped by two other layers, one on each side). CW proved to be a great component for film production, mainly due to its composition, rich in protein. The addition of gelatin to the multilayer film improved physical and mechanical properties in comparison to the neat PHA. Yu Y, Cui R, Wang X, Yang H. (2020) produced a cast monolayer with PLA

(3 g) dissolved in 45 mL of dichloromethane and then cast for 24 h. Firstly, the PLA films were immersed into HCl (hydrochloric acid) and rinsing with ultrapure water (Step 1). Then, the film substrates were immersed into Chinese yam polysaccharide solution and followed by rising with ultrapure water (Step 2). Next, the film was immersed into Chitosan solution followed by the same rinsing (Step 3). The multifunctional PLA film resulted in antibacterial and drug loading/releasing characteristic.

In the study reported by Andrade-Del Olmo et al., (2019) compression moulding and LbL were combined. PLA-ZnO (zinc oxide) nanoparticles were prepared by the solvent-precipitation process and moulded with a hydraulic press applying a pressure of 150 bar at 200 °C, for 4 min. After the activation of the carboxyl groups, the film was dipped into 2 g/L solution of Chitosan for 15 min, followed by acetic buffer solution rinsing. It was then dipped into a 2 g/L solution of 2-Carboxyethyl-βCD sodium salt incorporated with carvacrol; after that, the deposition cycle was alternated until 50 bilayers were obtained. This multilayer film improved the antibacterial and antioxidant properties.

Therefore, the development of multilayer films by the LbL technique is determined by factors including the type of adsorbing substances used, the number and sequence of layers incorporated, and the process conditions. Flexibility and simplicity in the use of various types of materials and the possibility to use active components remain as the potential advantages. However, the dip-coatings technique is a time-consuming process, which produces chemical waste and provides a small coated area for film formation. Although this limitation can be overcome by adopting spray assistance, it can be an issue for scaling up.

4.2. Casting

Solvent Casting is the most commonly lab-method used to produce bio-based monolayer films. A solution is formed with the polymer, the plasticizer and the solvent, commonly water. After starch gelatinization, the next step is drying, which can be conducted at room temperature or at a controlled temperature (30 to 40) °C. The latter step, however, is a time-consuming process, which hinders the scale-up for industrial applications. An alternative for the scale-up problem could be the tape-casting process, in which the support containing the film-forming solution permits drying control by conducting heat, circulating hot air (heat convection), and/or infrared (Siqueira et al., 2020). This technology requires a film-forming solution with adequate flow conditions under the blade and to concurrently prevent unwanted flow and sedimentation (Oliveira de Moraes et al. 2015). However, studies using this technologies are few in the literature (de Moraes and Laurindo 2018; Oliveira de Moraes et al. 2015).

To produce multilayer films by casting, one polymeric solution is cast on the surface of another polymeric layer previously produced (Tampau et al., 2020). The effectiveness of this method is greatly affected by the molecular interactions between the components in the solution and those on the contact surface (Tampau et al. 2020). In the literature, it is possible to find a wide variety of possible polymer combinations, with most of the studies using chitosan as one monolayer. Representative studies are presented in Table 2.

Bora & Mishra (2016) produced a bilayer film with casein monolayer (5 %) cast on Petri plates and further dried at 45 °C for 5–6 h. The other layer was formulated with pectin–sodium alginate prepared with 2.5 % pectin and 1.25 % sodium alginate, 0.01 % of $CaCl_2$ (Calcium chloride) solution and glycerol as plasticizer. Then, synthesized casein nanoparticle and casein-silver conjugated nanocomposite were incorporated in the inner layer (casein layer) and outer layer (sodium alginate–pectin layer), respectively. The addition of nanocomposite was observed to provide antibacterial property to the film and improved the light barrier. More recently, Bora & Mishra (2019) prepared a bilayer film using pectin–sodium alginate and casein with the incorporation of casein nanoparticles and silver nanoparticles, which improved the oxidative stability of almond oil during storage.

Some studies were performed with fish gelatin; for example, Jridi et al. (2019) prepared films based on grey triggerfish skin gelatin and agar , with or without vine leaves ethanolic extract (VLE). The mechanical properties were stronger in comparison to the gelatin and agar monolayers; moreover, VLE enhanced the antioxidant activity of the composite films. Nilsuwan K, Benjakul S (2018) also prepared bilayer films with fish gelatin and PLA. In their study, bilayer films showed lower water vapor permeability and less transparency than the neat PLA. Hanani et al. (2018) incorporated Pomegranate, papaya and jackfruit peel powders into fish gelatin solutions before being cast onto a polyethylene layer. The study showed the incorporation of fruit peel powders resulted in films with good water barrier and mechanical properties. Another bilayer film was produced with Olive flounder skin gelatin and PLA; the physical and barrier properties were enhanced in comparison to both monolayers (Lee & Song, 2017). In another study, a gelatin from cold-water fish and agar were used to produce a bilayer reinforced with TiO_2 (0.5,1, and 2 g/100 g) (Vejdan et al., 2016). The results showed the addition of TiO_2 decreased the water vapor permeability and tensile strength of the bilayers by more than 30%.

Gurler et al. (2020) used potato starch and PLA to produce a bilayer film. The main results showed the water vapor permeability, water uptake, moisture content, and solubility decreased with the bilayer assembly in compassion to the monolayers. In another study, hydroxypropyl corn starch (HPS) and zein (Z) solutions were prepared.

Firstly, HPS (6% w/v) film was cast and then dried at room temperature. Subsequently, zein solution (15% w/v) was poured onto the surface of HPS film, and then the bilayer film was dried at room temperature. The bilayer film presented smooth surface, water resistance and UV barrier property, and improved mechanical properties in comparison to the monolayers (Chen et al., 2019). Nogueira & Martins (2019) also evaluated bilayers assemblies with corn zein, wheat gluten and Hake protein isolate. Three different combinations were evaluated: Protein isolate (PI)/ Wheat Gluten (WG); Corn Zein (CZ)/ Wheat Gluten (WG) and Protein isolate (PI)/ Corn Zein (CZ). Firstly, an individual film was obtained, which was dried on Petri dish and a second film-forming solution was poured onto it. Finally, both were oven-dried with controlled temperature. The bilayers showed a total biodegradability around 40 days, and the bilayer PI/WG showed the best mechanical performance.

The casting demonstrated an interesting alternative to produce bilayer films with a variety of materials, such as starch, chitosan, casein, fish protein, wheat gluten, isolate protein; the addition of nanoparticles and essential oils provided additional benefits, exerting an active protection on the packaged foodstuffs. Good adhesion depends on the molecular interactions in the solution and on the surface. Most of the studies in the literature reported only the formation of bilayer assemblies, which may be a disadvantage in comparison to other technologies, e.g. LbL, which permits the formation of *n* bilayers. Moreover, the time-consumption step for evaporating water is always a drawback when scaling up this technology.

4.3. Compression Moulding

Compression molding is a process to shape plates or thick sheets (Kurtz 2019). Some advantages are low cost, short cycle time, high-volume production, dimensional accuracy, improved impact strength, and uniform shrinkage (Asim et al 2017). Two types of compression molding processes are possible: cold press technique, in which only pressure is applied, and hot press technique, in which both pressure and temperature are applied (Kurtz 2019). The process consists of heating a thermoset resin with pressure, in a mold cavity (Tatara 2017). The lower plate contains the resin powder or granules (Kurtz 2019). Then, the plates are pressed together. After cooling, the materials are removed from the mold.

Muller et al. (2017) produced a monolayer of crystalline PLA pellets compress-moulded in a hydraulic press at 200 °C and 100 bars for 4 min. The other monolayer was formed with starch, glycerol (30 g/100 g of starch), water (55 g/100 g of starch) and a small amount of Poly (ethylene glycol) PEG (0,5 g/100 g starch). Bilayer films were obtained through thermocompression of the monolayers by heating at 160 °C and 100 bars for 3 min and cooled to 70 °C. The main results showed that the bilayers exhibited lower oxygen permeability than the respective monolayers.

Requena et al. (2016) produced a bilayer with two monolayers of Poly(3-hydroxybutyrate-co-3-valerate) PHBV. The compression was performed at 160 °C for 4 min at 10 MPa followed by a cooling step. The PHBV monolayers obtained were sprayed with oils such as oregano, clove, carvacrol and eugenol, and were covered with another monolayer of PHBV. Then, bilayer films were compressed at 160 °C for 2 min at a 7 MPa followed by a cooling step of 3 min. The bilayer resulted in good layer adhesion and homogeneous structure, with increased mechanical, optical, barrier properties and antibacterial activity than the PHBV monolayer.

In the study performed by Ortega-Toro et al., (2015) three kinds of monolayer films were obtained: thermoplastic corn starch (S), thermoplastic starch with 5 % of Polycaprolactone (S95) and pure Polycaprolactone (PCL). The compression molding conditions were 80 ºC and 150 bars for 4 min and cooling cycle for 2 min. The authors obtained bilayer sheets (thickness > 0.250 mm) always with one PCL layer. Before the compression of the bilayers, 1 mL of distilled water (H_2O) or aqueous solutions containing ascorbic acid or potassium sorbate were sprayed. The main results showed the bilayer PCL/S95, with potassium sorbate showing the best mechanical and barrier properties and interfacial adhesion while having active properties.

The literature also presents the combination of two technologies, casting and compression moulding, resulting in bilayer assemblies with lower water vapor and oxygen permeability and improved mechanical performance. The incorporation of active compounds added value to these bilayers, inhibiting the growth of pathogenic microorganisms, and increasing the possibilities of application in the food packaging industry. Representative studies are presented in Table 3.

The compression molding process showed to be a successful technique by itself or combined with other techniques, such as solvent casting to produce bilayer assemblies, films or sheets, expanding its potential application. Some additives could be added to the interlayers to promote better adhesion between the monolayers and also to promote active characteristics.

4.4.Extrusion

Extrusion is a versatile technology that permits processing a wide range of raw materials. The high temperature and pressure during processing, and high-pressure drop in the extruder die results in physical and chemical transformations in the material, generating changes in their properties (Emin & Schuchmann, 2017). A co-extrusion process consists of an extrusion process in which two or more polymer materials are extruded together. Indeed, co-extrusion produces bilayer films with strong interfacial adhesion, which represent one of the challenges in the development of multilayer bio-based degradable films (Scaffaro, Sutera, and Botta 2018). However, to promote this adhesion, the use of an additive or special adhesion-improving processes, e.g., corona or gas treatment are needed, thus increasing the final cost of processing (David et al. 1994).

Scarfato et al. (2017) produced a multilayer consisting of a PLA–clay nanocomposite layer between two pure PLA layers by co-extrusion. The multilayer films were produced by a co-extrusion blown film apparatus with three single-screw extruders. The temperature profiles were from 190 to 200 °C, for the three extruders. The results showed the films had significant improvements: up to about 40%, in their barriers to oxygen and mechanical properties, and were more easily sealable at high temperatures (80–100 °C) in comparison to the pure PLA layers.

Scaffaro et al. (2018) produced a bilayer of PLA and *MaterBi,* which is a starch-based biodegradable thermoplastic polymer from Novamont S.P.A (Novara, Italy). In this study, PLA was blown into a single screw extruder at the temperature profile from 190 to 215 °C, die temperature of 190 °C and a screw speed of 60 rpm. The other polymer *MaterBi,* was blown into a single screw extruder at 120 to 175 °C with die temperature at 185 °C and screw speed at 60 rpm. The bilayer PLA/*MaterBi* coming from the two extruders were conveyed into the co-extrusion die. The experiment showed the PLA and *MaterBi* did not mix during preparation; the bilayer PLA/*MaterBi* resulted in higher stiffness and larger elongation at break in comparison to the monolayers. Messin et al. (2020) also produced a bilayer PLA/PBS consisting of a monolayer of PLA and another of a semi-crystalline poly (butylene succinate) (PBS). The ratio was PLA/PBS (80/20 wt%); each polymer was melted in an extruder at 190 °C and then spread through the multilayer system at 180 °C, the flat die at 170 °C and the chill roll at 40 °C. The resulting confined structure led to an improvement of its barrier performances of up to 30% for oxygen, 40% for water and 70% for carbon dioxide in relation to the monolayers (Messin et al. 2020).

Winotapun et al. (2019) produced a trilayer system (A/B/A) with PLA. An immiscible low-density polyethylene/polylactic acid (LDPE/PLA) blend was set as (B) layer and LDPE was used as (A) layers. The compositions of PLA in the B layer were varied by up to 50 wt%. The extrusion process for the three was performed with the same temperature profile from 40 to 195 °C, die temperature of 200 °C, and a screw speed of 60 rpm. Multilayer films containing 40 and 50 wt% PLA showed a reduction of oxygen permeability of ~ 20% and 43%, respectively, compared with the single LDPE film.

Mazerolles et al. (2020) also produced a trilayer system with low-density polyethylene (LDPE) and thermoplastic starch (TPS). Potato and corn starches were plasticized with glycerol and blended with LDPE using a twin-screw extruder, the TPS fraction was varied from up to 80 wt%. The TPS/LDPE blend was used as one layer and pure LDPE as the outer layer. Clays were added to the TPS phase at concentrations of up to 5 wt%. Adding clay was found to improve the films processing, with a higher oxygen barrier, while maintaining similar mechanical properties, in comparison to pure LDPE.

Co-extrusion is an interesting alternative to produce bilayer assemblies with good scale up. The viscosity of the polymeric matrixes is crucial as they pass through the die, otherwise mixing can occur, instead of adhesion. This adhesive property could be improved by methods that increase not only the properties but also the final cost of the process. At the industrial level, polymeric materials, such as polyethylene, polypropylene, polyamide and their combinations are currently produced in the bio-based systems; most of the studies in the literature reported the use of PLA in one monolayer probably due to the excellent processability, reasonable mechanical performance and transparency.

4.5. Electrospinning

Electrospinning is a technique that utilizes an electrostatic force to turn polymer solutions into nanofibrous films (Wang P, Li Y, Zhang C, Que F, Weiss J 2020). During this process, a polymer solution extruded from the spinneret forms a semispherical droplet at the tip of the needle connected to a high voltage power supply (Wang P, Li Y, Zhang C, Que F, Weiss J 2020). When reaching a critical value, the charged droplet first deforms and eventually overcomes the surface tension causing a polymer jet to be ejected, which is then deposited on a collector in the form of randomly-oriented nanofibers (Wang P, Li Y, Zhang C, Que F, Weiss J 2020). The main advantages are high surface area/volume ratio (Tampau, González-Martínez, and Chiralt 2020). Some advantages of this technique include the simplicity of the procedure and relative low cost. This technique has the ability to control many factors during processing (Dahlin, Kasper, and Mikos 2011). However, this can be a challenge for scale-up applications; the main difficulties and challenges include large-volume production, partially overcome by the development of multiple-needle (Xue et al. 2019). However, environmental issues have to be fully considered when scaling-up; in fact, solvent evaporation into the environment could result in an environmental burden (Xue et al. 2019).

Consecutive electrospinning was utilized to produce a multilayer film with ethyl-cellulose nanofibers as the outer layer and curcumin-loaded gelatine nanofibers as the inner layer, with a voltage of 15 kV at a distance of 10 cm from the syringe tip and a constant volume flow rate of 1 mL/h. The outer layer decreased the water vapor permeability and improved the water contact resistance of the hydrophilic inner layer. The antioxidant activities of the released curcumin from the multilayer film were well retained within 96 h (Wang et al. 2020). In another study, Balik et al. (2019) prepared a multilayer film with pectin-based films as an interlayer between two electrospun layers of PHBV. Firstly, a solution of Pectin, Polyethylene oxide (PEO_{2000}), glycerol; a surfactant (2 wt %) was electrospun at a flow-rate of 3 mL/h and the voltage ranged from 16 to 20 kV. Then, PHBV layers were electrospun at a voltage of 10 kV, at a tip-to-collector distance of 15 cm, and flow-rate of 6 mL/h. The multilayer film was then pressed at 160 °C for 10 s. Adequate barrier properties are the main result .

Some studies reported the combination of casting-electrospinning techniques. Bharathi et al. (2020) produced chitosan cast films with PEG 400 at the appropriate concentration of up to 25% (w/w of polymer). To produce the bilayer active film, the chitosan cast solution was attached to the 20 cm x 20 cm stainless steel collector and the zein was directly electrospun on the chitosan film at a flow rate of 0.4 mL/h, 1, 12 kV voltage and 10-cm needle to collector distance. The main results showed this bilayer film can be used as an effective anti-browning package.

Gelatine, glycerol and microcrystalline cellulose solution was cast, then electrospun with polycaprolactone and black pepper oleo resin as a natural extract. The multilayer system increased the mechanical properties and decreased the barrier properties unlike the monolayers of gelatin and polycaprolactone, besides inhibiting the growth of *Staphylococcus aureus* (Figueroa-Lopez et al. 2018). In another study, PLA was cast and hydroxypropyl methylcellulose fibres were collected by electrospinning. The multilayer system decreased, which suggests a possible application for packaging light-sensitive foods (Aydogdu et al. 2019). A tri-layer system was prepared by combining casting-electrospinning techniques. Gelatine out layers were fabricated by solvent casting and dextran film, with or without propyl gallate, was then electrospun in the interlayer. For the electrospinning process, the solution was placed in a 2.5 mL syringe at a speed of 0.5 mL/h to the syringe tip where a voltage of 15 kV was applied. The multilayer assembly showed a good physical barrier and extended the release of propyl gallate, thus improving its antioxidant ability (Wang P, Li Y, Zhang C, Que F, Weiss J 2020).

In some other studies, electrospinning is combined with the compression moulding technique. Wheat gluten was mixed with glycerol and then compress-moulded at a pressure of 37.92 MPa for 12 min at 100 °C. A commercial polyhydroxybutyrate (PHB) and a polyhydroxybutyrate-covalerate copolymer with 3 % valerate content (PHBV3) were collected onto both sides of the plasticized wheat gluten film by electrospinning process at 80 mL/h of flow rate. Finally, the systems were compressed at 145 or 160 °C for 1 min. The addition of the outer layers improved the mechanical properties, especially Young's modulus, which increased up to ~40 % for the three-layer films (Fabra, López-Rubio, and Lagaron 2015). Arrieta et al. (2019) produced a multilayer based on a compression moulded PHBV as the out layer, while antioxidant electrospun fibers based on PLA, poly(3-hydroxybutyrate) (PHB) and Oligomeric lactic acid blends formed the inner active layer. The bilayer systems obtained showed antioxidant effectiveness, yet no increase in the mechanical properties was observed. Castro Mayorga et al. (2018) produced a bilayer consisting of a layer of compression-molded PHBV3 (3% mol valerate) covered with a layer of an active electrospun fibers mat produced from CuO nanoparticles and PHBV18 (18% valerate). As a result, both water vapor and oxygen barrier properties were slightly more enhanced than the neat PHBVs without CuO, and a negligible effect was observed in mechanical properties.

Finally, a combination of extrusion and electrospinning was reported. PLA pellets were extruded at temperatures from 195 °C to 210 °C. The PLA film was placed on the collector and a PLA solution with antioxidant gallic acid (GA) was electrospun for 1, 2, and 3 h under a steady flow-rate of 2.2 mL/h. Then, another PLA film was placed on the other side, and the resulting whole structure was finally post-treated at 150 °C without pressure. Although the bilayer (PLA/GA) fibres easily delaminated, the multilayers (PLA/GA/PLA) showed adhesion between layers and high transparency, offering a high sustained release (Quiles-Carrillo et al. 2019). In the study performed by Estevez-Areco et al., (2019) the outer layer consists of a film of thermoplastic starch and ZnO nanorods particles (TPS-ZnO) obtained by extrusion with screw diameter of 16 mm, screw speed (80 rpm) and temperature profile from 90 to 140 °C. The inner layer was an electrospun mat of poly (vinyl alcohol) containing rosemary polyphenols (PVA-RE). Bilayer films were hot-pressed at 35 kPa and 130 °C for 5 min to improve adhesion. The results showed the incorporation of both PVA-RE nanofibers, and ZnO nanorods resulted in a material with more improved barrier and mechanical properties than the neat thermoplastic starch matrix.

To sum up, electrospinning showed an interesting alternative to produce multilayer films. Most of the studies reported the combination of electrospinning with other techniques, e.g. casting, compressing moulding or extrusion. The possibility of adding fibres and/or active compounds enhances the performance of the multilayer assemblies. However, the systems employed were at lab scale and this is a major drawback. Furthermore, the environmental concern due to the solvent evaporation in the environment is an important issue to consider for industrial applications.

5. Future perspectives

After all the previously reported information , it can be seen that each treatment shows some advantages and disadvantages, which have to be considered to produce the most suitable film for each specific application. Table 4 briefly shows some advantages and disadvantages of the process employed to produce the multilayer systems discussed in this review.

Most of the studies reported herein were produced by well-known lab technologies, such as casting, Layer-by-Layer deposition, electrospinning and/or the combination of them. Although casting is a well-known lab method characterized by its simplicity, the high time consumption and the need to evaporate large amounts of solvents are some challenges to overcome when planning to scale-up. Moreover, most of the studies produced under this technology report no more than three layers. LbL deposition or electrospinning permits the construction of more than 100 layers; however, these technologies produced chemical waste, which at an industrial scale may not be interesting due to recent trends towards more sustainable eco-friendly techniques, with minimal waste production.

In the near future, techniques that facilitate the scaling-up, such as extrusion and compression moulding should gain more interest. Extrusion is the most used technology to produce plastics at the industry level with a huge variety of thicknesses (films and sheets) and is thus a promising approach to produce bio-based plastics. However, there are few studies related to this technology, probably due to the high cost of the equipment. Evaluating the cost production and technical feasibility are also very important.

Concerning the materials, they generally resulted in increased mechanical and barrier performance when compared with their respective monolayers, which increases their possible application in different areas.

Another challenge associated with multilayer films is the evaluation of the environmental impacts and the endlife of these materials. Recycling multilayer films is still a crucial problem due to the large variety of monolayers used, with their particular processing properties, added to the lack of a system to collect these materials. In current conditions, biopolymers could potentially lead to the contamination of conventional plastic collectors, affecting the quality and physical integrity of the resulting materials (Soroudi and Jakubowicz 2013).

Their degradability could be a further problem to be overcome, since different interlayers possess diverse properties and the biodegradability of one could be affect by the presence of another. When incorporated, some antimicrobials can delay the process of degradation, which could vary depending on the microorganism population (Hernández-García et al. 2021). Further studies regarding this issue must be performed. Therefore, further consideration and studies are needed to produce a more suitable combination of biopolymers.

6. Conclusions

In this study, the multilayer strategy to produce bio-based plastics under different production processes was reviewed. The key for multilayers assembly is the bonding between layers; therefore, different technologies were explored to produce the best adherence between monolayers. The resulting multilayer assemblies show different characteristics, and, thus, many applications in different industries are possible. In general, multilayer assemblies enhanced mechanical properties and decreased barrier properties, in comparison with their respective monolayers. Moreover, the addition of antimicrobial or antioxidant into the multilayer structure provides an additional benefit which increases the possibilities for applications in diverse areas.

Some technologies studied are adequate for producing multilayer at lab scale, but are difficult to scale up for industrial production. Therefore, scale-up, cost and technical feasibility, life-cycle assement and, specifically, their degradability are still to be studied.

In conclusion, researches for developing multilayer bio-based plastics and the more suitable process production are in progress; however, there is still a long path to achieve materials with enhanced performance that can prove to be a great environmental-friendly alternative to conventional plastics, being biodegradable, sustainable and renewable.

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Figure Caption

Figure 1.

Schematic representation of the main methods used to produce bio-based multilayer films.

Figure 2.

Studies involving multilayer films produced with biopolymers in the last 5 years. **A.** Distribution by production processes and **B.** over the years. The literature search was performed on the Web of Science® database on 22 September of 2020.