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A second life for fruit and vegetable waste: a review on bioplastic films and coatings for potential food protection applications

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In recent decades, significant progress has been made on the development of low environmental impact plastic materials, as alternatives to conventional plastics for food packaging. Research has focused on the engineering of renewable resources of animal or vegetable origin that are rich in polysaccharides and proteins, to produce green bioplastic materials for food packaging, with good mechanical and gas barrier properties. Furthermore, incorporating natural antimicrobials, antioxidants, and pH-sensitive substances in the new eco-friendly materials, smart and active green packaging can be developed. Recently, the preparation of bioplastics and biocomposites directly from the processing of agro-food residues *via* hydrolysis or digestion was proposed for the production of new added-value products that comply with zero waste and circular economy principles and are expected to impact the future of food packaging significantly. This review aims to revise the various fruit and vegetable agrowaste-based bioplastic and biocomposite systems developed so far, with potential applications in food protection and shelf life extension. The vegetal lignocellulosic and non-lignocellulosic agrowaste composition, processing methods, and properties of the developed biomaterials are addressed. The obtained biocomposites, rich in natural polymers, as cellulose, pectin, starch, zein, *etc.*, can actively protect the packaged food against oxidation or microorganisms, as long as they preserve the raw materials' phytochemicals in their composition. We focus on simple and easily scalable procedures that either involve green solvents or require low-energy, and lead to films for food packaging or suspensions intended to be applied as coatings directly on fruit or other foodstuff surfaces. All the previously mentioned aspects are extensively reviewed in this manuscript, mainly considering the literature reported during the last five years including the research works of the authors in the field.

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1 Introduction

1.1 Current situation in food packaging: towards new biomaterials

Nowadays, food packaging is an indispensable part of the food industry. Food packaging is mainly used to establish a barrier between the food and the environment in order to provide mechanical protection and to reduce food contact with spoilage factors, such as microorganisms, oxygen, and UV-light, as well as to avoid losses of flavors and odors, to extend food shelf life and quality.[1] Additionally, food packaging has several other functions, including marketing, information on the product's ingredients and expiry.[2]

From the second half of the 20th century, petroleum-based polymers increased in popularity and ended up dominating the food packaging industry thanks to their excellent properties, versatility, and low price.[3] Materials such as polyethylene (PE), polypropylene (PP), and polyethylene terephthalate (PET) are nowadays the most used in the packaging sector, despite their high contribution to the accumulation of plastic waste in the environment. These products originate from non-renewable resources and, most importantly, are non-biodegradable. Their uncontrolled accumulation has raised profound concern about their deleterious effects to the environment. In fact, when they end up in landfills or the oceans, it takes hundreds of years to be biodegraded.[1,4] The alternative of their incineration for energy recovery has a severe environmental impact, including the generation of toxic airborne particles and greenhouse gas emissions.[2] Although the recycling of such non-biodegradable polymers comes as a better alternative, the gradual chemical deterioration during that process limits the further application of recycled plastics in food

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packaging. Finally, many of the current plastic packaging items are made by combined polymers, making their recycling technologically challenging and non-economically sustainable. For example, within Europe, one of the best global scenarios regarding the actions against plastic pollution, 24.9% of plastic waste is disposed of in landfills, 42.6% is used for energy production and 32.5% is recycled.[5] The immense contribution of plastic packaging products to plastic waste generation is mainly due to their very short lifetime, about 1 year in average, that forces a very quick turnover of materials with lack of economically viable recycling.[6,7]

In this scenario, more than 60 countries have issued prohibitions on the use of plastic products, such as single-use plastic bags, intending to stop the increasingly severe environmental pollution.[8] These prohibitions are in line with the Directive (EU) 2019/904 of the European Parliament and of the European Council of 5 June 2019 on the reduction of the impact of certain plastic products on the environment.[9] Furthermore, the European Commission guidelines on single-use plastic products, mainly connected to food protection and consumption, have recently been published in accordance with this Directive (May 31, 2021).[10]

The above-described situation highlights the immediate need to reduce the use of traditional plastics and a great necessity for new sustainable materials capable of replacing plastics in the food packaging industry and in other short-lived applications. These alternative materials can be considered sustainable only if they have positive implications simultaneously on the environment, economy, and society. Bioplastics that are made of renewable resources, preferably wastes, that can be recyclable and biodegradable at the end of their life-cycle fulfill this requirement,[1] since they contribute to the reduction of plastic waste generation, of nonrenewable raw materials dependence, and of water and energy usage.[2] The use of vegetable wastes as raw materials for bioplastics preparation has the additional potential to reduce greenhouse gas emissions, since plants uptake carbon dioxide from the atmosphere during their growth and convert it into biomass thanks to the photosynthesis.[11] Furthermore, plant biomass offers immeasurable potential for bioplastics preparation through methods that include, but are not limited to, the extraction and isolation of polymers, the possibility to obtain monomers for further synthetic routes and the possibility to disassemble, mix and reassemble the entire biomass to develop blends and composites. Although this review focuses mainly to the latter processing methods, all the above methods have great potentiality and lead to a wide variety of materials and the possibility to tune their properties for specific applications. Thus, they can be the ideal candidates for replacing traditional polymeric packaging in all its forms, *i.e.* rigid, flexible and coatings. More details about the chemistry of the materials prepared from vegetable waste are introduced in the following section.

The bioplastic packaging needs to maintain its properties unaltered from the moment of the introduction of the food within it, till the moment of its removal for consumption. Successively, it is highly required that its biodegradation starts as soon as it is disposed of, and happens in short time.[12] The biodegradation can be triggered by external factors such as humidity, temperature, changes in pH, and UV-light exposure, in the presence of microorganisms or enzymes. Research efforts are being made to improve the end of life compostability of the few already commercially available sustainable biopolymers, such as polylactic acid (PLA), polybutylene succinate (PBS) or polyhydroxyalkanoates (PHAs). These materials are produced from plant biomass through various sequential processes that will be mentioned further down, are rapidly biodegradable in specific conditions (industrial composting sites, with temperatures around 60 °C) and slowly biodegrade over the years when they end up dispersed in the environment, although PHAs are marine-degradable.[13] New policies should be implemented to ensure their correct collection and composting, while governments worldwide need to support the increase, expansion and improvement of the industrial compost sites.

On the other hand, biocomposites produced by the direct transformation and reorganization of plant biomass from agrowastes are more easily compostable at environmental conditions, and can possibly be managed together with the organic waste produced at homes. Furthermore, antimicrobial and antioxidant molecules that are present in the biomass of the agrowastes can provide functional properties to such biocomposites, that can help extend food shelf life and quality when used for food packaging.

Finally, it is worth mentioning that sustainable solutions to conventional non-biodegradable plastics could also come from microalgae exploitation. In fact, microalgae can be used to biovalorize food wastes and food processing waste waters to produce proteins, lipids and carbohydrates, but can also be transformed through reorganization upon solvent processing into composite bioplastic films.[14–16]

In this manuscript, we review the bioplastics and biocomposites obtained from the processing of biomass from industrial vegetable agro-food by-products, consistent with zero waste and circular economy models, as pictured in Fig. 1, focusing mainly on biocomposites obtained from the biomass deconstruction, separation and reconstruction under a different form.

1.2 Agro-food waste components and their potentiality for new biomaterials in food packaging

The life cycle of a typical food item can be summarized in four phases: (1) production, (2) processing, (3) distribution, and (4) consumption. Food loss can occur at every step of the supply chain and also occurs when food is removed from the chain. According to the Food and Agriculture Organization of the United Nations (FAO), 13.8% of all food produced worldwide is wasted between the harvest on-farm, transport, storage, processing, and wholesale stages.[17] For the scope of this manuscript, as food waste we adopt the definition given by the FUSIONS EU project,[18] that is "any fraction of food and inedible parts of food removed from the food supply chain to be recovered or disposed of".[19]

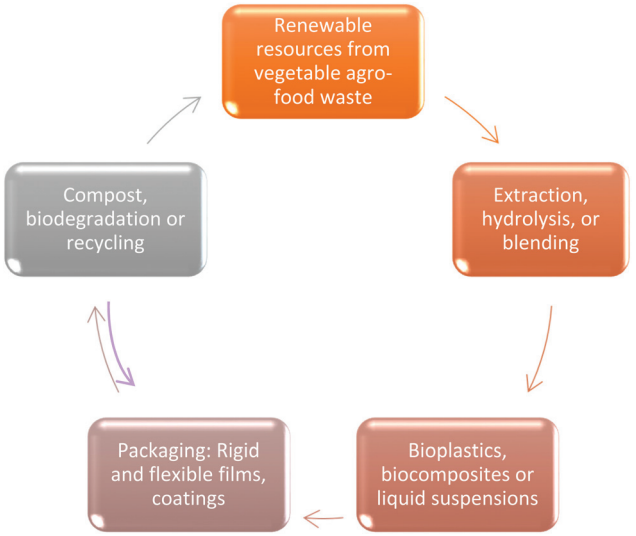

Fig. 1 Life cycle of an ideal system for packaging based on the circular economy of agro-food waste.

The generation of edible food waste should be reduced by taking precautionary measures at each level from its production to its consumption. Since the growing world population demands more food, minimizing the edible waste could be a viable solution, reducing intensive agriculture. Regarding the inedible discards, there is an extreme need for adequate practices and policies for their management and reuse.[20] The inedible parts of agro-food production could be the ideal biomass source for the production of the new sustainable bioplastics. Indeed, agricultural processing by-products such as husks, peels, straw, seeds, and pomace, constitute a reservoir of carbohydrates, proteins, lipids, and phytochemicals,[21,22] all invaluable components for new biomaterials. Next, we present analytically all these components of the plants and where they can be found within the plant.

1.3 The plant cell wall

Most of the natural polymers are found in the plant cell walls, playing a fundamental role: they are the key elements that control the wall's resistance, stiffness, and flexibility. Precisely, the cell wall consists of a network of cellulose microfibrils embedded in a highly hydrated amorphous matrix of other complex and heterogeneous non-cellulosic polysaccharides, hemicelluloses, and pectins. As shown in Fig. 2A, there are two types of vegetable cell walls: primary and secondary. The primary walls are typical of growing cells, which require wall flexibility and are generally poorly specialized. Secondary walls form after growth has ceased, they are thick, inflexible, and highly defined in structure and composition.[23] Between the walls of neighboring cells, is located the middle lamella, which contains pectin and proteins.[24] In addition, vascular plants present a hydrophobic layer called cuticle at their plant-environment interface. It consists of a cutin polymer film with embedded intracuticular waxes, whose main function is to prevent uncontrolled water loss. Wax constituents include long chain hydrocarbons, such as alkanes, primary alcohols, aldehydes, secondary alcohols, ketones, esters, and may also contain triterpenoids, flavonoids, and/or phenolic lipids.[25]

Although both types of walls are based on cellulose microfibrils, the components of the amorphous phase vary widely throughout the plant kingdom. Furthermore, cell walls are dynamic entities, which can change their structure and composition during plant development and in response to abiotic and biotic stress.[26] The primary wall is made up of polysaccharides such as cellulose (Fig. 2B), hemicelluloses (Fig. 2C), pectins (Fig. 2D), a small part of structural proteins, and a significant part of water (between 75 and 80%). Hemicelluloses bind cellulose, and together with pectin, they help bind its fibers and prevent the structure from collapsing. The secondary cell wall consists of cellulose, hemicelluloses, and in some cases, lignin (Fig. 2E) with a minimal amount of water (5%).[27] Raw materials that include a high content of these three components are called lignocellulosic biomass and include non-commercial material traditionally left on site after harvesting of crops such as trunk, fiber, sugar cane bagasse, plant stalks, vines, hulls, leaves, vegetable matter, sawdust, mill residues, low-quality wood, tops, and limbs.[28]

1.3.1 Cellulose. Cellulose (Fig. 2B) is the most abundant polysaccharide on planet earth.[29] It is a linear polymer of 7000–15 000 glucose units linked by β-1,4 bonds in which each glucose residue has a rotation of 180° with respect to the next, resulting in a polymer whose repeating unit is the disaccharide cellobiose.[30] These units form long unbranched chains that interact through hydrogen bonds, creating structures of high crystallinity called fibrils, which are then grouped to form microfibrils and that in the presence of hemicellulose and lignin are assembled into the well-known natural fibers. In this way, cellulose fibers have a hierarchical structure with areas of high crystallinity (55–75%) and high chemical and mechanical resistance, connected by amorphous areas, more susceptible to chemical and enzymatic attack.[27]

1.3.2 Hemicellulose. Hemicellulose (Fig. 2C) is a heterogeneous set of branched polysaccharides more complex than cellulose and with lower molecular weight, usually formed by 500–3000 monomer units.[28] Chemically, these polysaccharides are composed of combinations of monosaccharides of five (xylose, arabinose) or six carbon atoms (glucose, mannose, galactose). These polysaccharides act as a support matrix for cellulose microfibrils binding to them and, when present, also binding to lignin.[31] Among the carbohydrates usually included in the category of hemicelluloses are xylan, xyloglucan, mannan, glucomannan, and galactoglucomannan, and their occurrence in the cell walls varies with the plant species, among other factors.[27]

1.3.3 Pectin. Pectins (Fig. 2D) play a key role in controlling cell wall flexibility, cell proliferation and growth.[32] They are made of heterogeneous polysaccharides that mainly have α-(1,4)-D-galacturonic acid in their structure and, to a lesser extent, neutral sugars such as rhamnose, galactose, and arabinose.[27] They consist of a series of structurally different

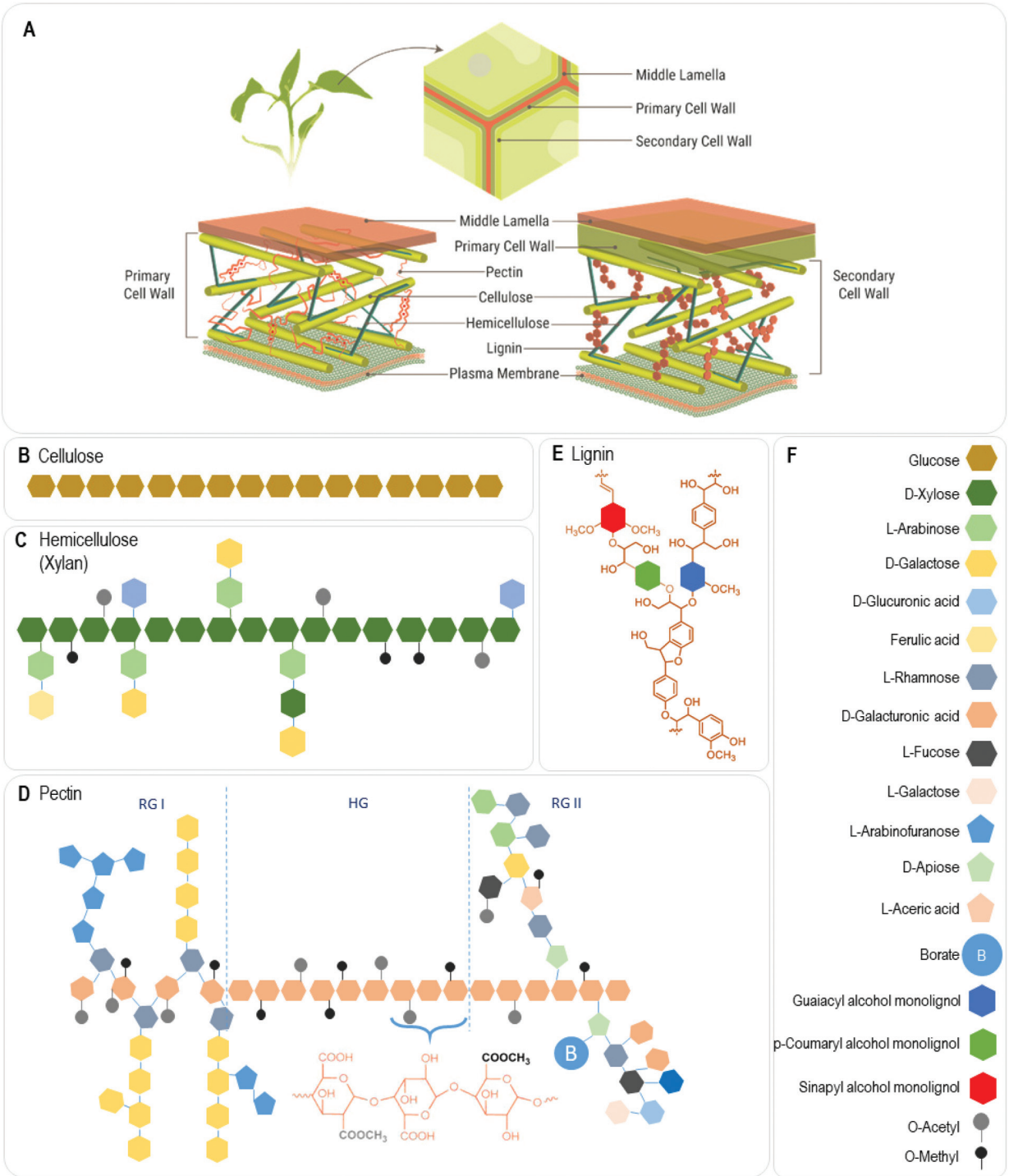

Fig. 2 Schematic representation of plant cell walls and their main polymeric components. (A) Structure and principal components in primary and secondary plant cell walls. (B) Scheme of cellulose polymer's structure. (C) Scheme of xylan, a hemicellulose, structure. (D) Scheme of pectin polymer's structure. The domains homogalacturonan (HG), rhamnogalacturonan I (RGI), and rhamnogalacturonan II (RGII) are represented in the scheme and the chemical structure of HG backbone was also included to show *O*-methyl and *O*-acetyl substitutions. (E) Scheme of lignin polyaromatic polymer. (F) References for figures understanding.

domains from which they can be distinguished: homogalacturonan (HG), rhamnogalacturonan I (RGI), and rhamnogalacturonan II (RGII), among other less frequent ones. The first HG domain is the most abundant and important in the union of divalent and trivalent cations. It represents ~65% of the pectins and is made up of galacturonic acid monomer units linked by α-(1,4) bonds. It is partially methylated at the C-6 carboxyl groups, and it can be *O*-acetylated at O-2 or O-3.[24,30] The

RG I domains represent 25 to 30% of pectins. They have as repetitive unit, dimers of α-(1,4)-D-galacturonic acid and α-(1,2)-L-rhamnose, which are partially substituted with side chains containing linear and branched residues of α-L-arabinose and/or β-D-galactose, showing high heterogeneity according to plant sources.[30,31] RG II are the least abundant but most complex and branched domains of pectin, representing approximately 10% of the total. They have a main chain of about 8 residues of α-(1,4)-D galacturonic acid with four side branches containing 12 different types of sugars linked by at least 20 different forms.[24]

Pectins are transported to the wall in highly methyl esterified forms and selectively de-esterify to control matrix stiffness by forming gels in the presence of calcium or boron ions that chelate with charged carboxylic groups forming egg box structures.[29,32] Therefore, they show gelling capability, which was explored to prepare hydrogels, coatings, and cross-linked films.[33–36] Besides, they were also capable of being processed by melt extrusion in the presence of a plasticizer, showing a thermoplastic characteristic.[37]

1.3.4 Lignin. Lignin (Fig. 2E) is the most abundant aromatic polymer in nature. It is found in most vascular plants, where it can represent 40% of the plant wall. It is made of aromatic heteropolymers derived from three monomers: the *p*-coumaryl alcohol (4-hydroxycinnamyl), coniferyl alcohol (4-hydroxy-3-methoxycinnamyl) and sinapyl alcohol (4-hydroxy-3,5-dimethoxycinmyl) that bind forming a three-dimensional network of different types of links, resulting in an irregular and complex pattern.[38] It is found mainly in the secondary plant cell, where it holds the cellulosic fibers together, conferring rigidity and impermeability to the plant, and finally, it is resistant to biodegradation, protecting the wall from most microbial attack.[31]

1.4 Other plant intracellular biopolymers

1.4.1 Starch. Starch is a widely known biopolymer used in material science for the production of biodegradable materials. It occurs intracellularly in the amyloplasts of plant cells, where it serves as a source of carbohydrate reserve for plants. It is synthesized in semicrystalline granules, whose morphology and size are specific for each plant species, and can adopt a round, oval, ogival, or lenticular shape while its sizes range from submicron to 100 μm in diameter. These granules, however, have an internal structure that is broadly common to all of them.[39] Starch is made up of two polyglucans: amylose and amylopectin. Amylose consists of glucose residues connected through α-(1,4) bonds forming long and mainly linear chains with a few α-(1,6) branches. Amylopectin, which is the main component, has the same basic structure but has considerably shorter chains and many more ramifications α-(1,6).[39] Starch has been widely used for the preparation of thermoplastic materials by combining it with a plasticizing agent.[40,41] Thus, plant residues rich in this polymer have a high potential for processing as conventional thermoplastic polymers.

1.4.2 Proteins. Proteins represent another group of important plant compounds. A wide variety of proteins can be found in plants, with many different functions.[42] Storage plant proteins of nutritional value are made of 20 different amino acids and could be classified according to their solubility using the Osborne classification: albumins are water-soluble proteins, globulins are soluble in dilute salt solutions, prolamins are soluble in alcohol and alcohol-water mixtures, and glutelins are soluble in diluted acidic or basic solutions.[43] In tissues such as leaves, proteins constitute only a minor amount, for instance, only 1–3% of the dry mass in lettuce leaves. On the other hand, seeds are very rich in storage proteins that are needed to sustain their germination and the growth of the plants at the initial stages. In seeds, protein amounts are significantly higher, up to 40% of the dry weight. In particular, they comprise 40% of soybeans, 9–12% of corn kernels, 25% of peanuts, and 20% of sunflower seeds.[44–47]

Vegetable derived proteins are often found as a byproduct of food processing, either because they have poor nutritional value or because they are the result of refining of legumes. These proteins, often with the addition of some plasticizers, have been proposed for the production of bioplastics. For example, soy proteins (SP) and wheat gluten (WG) are among the most studied proteins for the production of bioplastics because of their wide availability and low price. SP result from the processing of soy beans after the extraction of the oil. Their main constituents are non-polar aminoacids such as glycine, proline, alanine, valine, acidic amino acids such as aspartic and glutamic acid, and finally basic amino acids such as lysine and arginine.[48] Despite their good nutritional value, not all the soy proteins produced are consumed, and a significant portion ends up being discarded. To be processed into bioplastics, soy proteins benefit from the addition of plasticizers such as glycerol or water.[48] WG is a relatively cheap protein obtained from wheat processing to obtain starch. Commercially available WG has high protein content (>75%, the rest being starch and lipids) that is due to mostly two proteins: gliadins (that are low-molecular-weight) and glutenins (high-molecular-weight).[49,50] Both proteins are prolamine proteins and are storage proteins whose function is to help the germination of the seeds. When combined *via* S–S bridges, gliadins and glutenins create a strong network with good viscoelastic properties.

Other examples of less known proteins obtained from biomass are zein and kafirin. Zein is a prolamine protein with poor nutritional value and so has limited uses as an ingredient for foodstuff. It is obtained from the processing of corn, in which it has a function as a storage protein providing nitrogen for growing kernels during corn germination and it is composed of glutamine, leucine, proline, and alanine aminoacids.[51] Zein proteins are alcohol soluble and form films upon casting, but, similarly to other proteins, their films are usually brittle and fragile, and a plasticizer is needed to provide flexibility.[52,53] Similarly, Kafirin is the family of storage proteins in sorghum and are classified as prolamines. Their molecular weight is between 12 961 Da and 27 000 Da and they are comprised of mostly non-polar amino acids such as proline.[54,55] Kafirins are known to be the most hydrophobic

prolamines.[56] Kafirins are relatively less explored for both food and non-food applications because of the low sorghum production. Despite being the fourth cereal produced worldwide, sorghum represents only 3% of the total cereal production.[56] Because of the high hydrophobicity and poor digestibility, kafirins are better suited for non-food applications and are studied for applications ranging from adhesives to bioplastics to biomedical devices.[57]

1.5 Plant intracellular functional phytochemical compounds

Phytochemicals are plant-derived chemicals. Some of them, called nutraceuticals, can provide health benefits for consumers either in food or in isolation.[58] These benefits translate into better nutrition, treatment and prevention of diseases, and delayed aging. They could also reach consumers through packaging, edible or not, based on fruit and vegetable residues.

In addition, when phytochemicals are incorporated into the food packaging, they can actively protect food, extending its shelf life and giving information about its quality.[59–61] For instance, phenolic compounds provide antioxidant activity, which in some cases can be used to extend the shelf life of food. Besides, some of them also have antimicrobial action and, together with essential oils (EOs), constitute the most commonly used type of phytochemicals for the development of active and sustainable food packaging.[62] EOs are mixtures of 20 to 60 different secondary metabolites. Among those, 2 or 3 components predominate, generally terpenes and terpenoids, while other aromatic and aliphatic compounds such as aldehydes and phenols are found in smaller quantities. They are characterized by an intense odor and flavor that vary depending on their constituents and they play a vital role in the plant defense due to their antibacterial, antifungal, and antiviral action.[63] These properties make them good candidates to replace chemical preservatives and can be included as active components in food packaging materials.[62] In particular, compounds such as linalool, thymol, carvone, carvacrol, citral, and limonene are regulated by the European Commission as flavorings for food products and have been categorized as "generally recognized as safe (GRAS)" ingredients by the Food and Drug Administration.[64]

It is worth mentioning that the processing of the vegetable wastes can influence the chemical and functional stability of their phytochemicals, so it is a parameter that must be considered.[63] Detailed information on these aspects can be found in the literature.[65]

2 Brief review of the methods of transformation of agrowastes into bioplastics

The most widespread and traditional way to obtain bioplastics from agro-food waste is to extract and purify natural polymers, monomers, or other compounds through quite complex processes briefly mentioned below.

Bioplastic films, intended for various applications among which also food packaging, are then obtained mainly through techniques such as blending, solution casting,[66–68] chemical synthesis starting from the monomers,[69,70] to obtain biopolymers that can be processed by thermomechanical processes like extrusion.[71–73] Concerning bioplastic coatings, liquid solutions containing biopolymers and active phytochemicals can be applied onto substrates, *i.e.* food, either by dipping or casting or spraying techniques. Dipping is suitable when the substrate has an irregular surface, casting when the coating solution is more viscous, while spraying is more appropriate when only one side of the product is supposed to be coated.[74,75]

Many of the extraction processes of the polymers present in the vegetable cell wall are done with acidic or alkaline solutions or both. For instance, cellulose nanocrystals (CNC) or microcrystalline cellulose (MCC) can be recovered from agro-food residues by a combination of acidic (H_2SO_4) and alkaline (NaOH) hydrolysis treatments.[76] In this process, usually carried out on lignocellulosic biomass, hemicelluloses and lignin can be obtained as byproducts.[77,78] Furthermore, pectin polymer found in non-lignocellulosic biomass, is usually obtained by extraction from citrus and apple peels in hot water or hot diluted acid solutions, followed by an isolation step through alcohol precipitation.[79,80]

Even though these extraction methods are well established, they present some challenges, like the disposal of the acid compounds produced after the acid treatment step. Therefore, different innovative extraction processes are under study and investigation. One of these is the autohydrolysis process, which allows obtaining, for instance, MCC with similar results to acid hydrolysis, taking advantage of high pressure and temperature, avoiding the use of sulfuric or other strong acids.[81,82]

Intracellular polymers, such as proteins and starch, can also be obtained through acid-alkaline treatments but also through solvent-assisted extractions. For instance, proteins can be extracted by dissolution in an alkaline environment and subsequent precipitation at their isoelectric point with the addition of concentrated solutions of mineral acids like hydrochloric acid and sulfuric acid.[83] Alternatively, some proteins are obtained by solvent-assisted extractions. For example, α-zein proteins and a small amount of β-zein proteins can be extracted with 80–85% (v/v) ethanol or 2-propanol, while α, β, γ, and δ-zein proteins are extracted by combining an alcohol with a reducing agent that contributes to the disulfide bonds break and release of zein proteins.[45] Similarly, kafirins are usually extracted with ethanol and a reducing agent such as sodium metabisulfite, although this method is usually preceded by an enzymatic pretreatment.[84]

Starch, another important intracellular polymer, is mainly recovered using wet extraction processes, where different extraction liquids can be utilized to dilute starch in the liquid phase. Sometimes sodium sulfate solution is used to promote the separation.[85] Besides, other innovative methods like ultrasonically-enhanced wet extraction or microwave radiation have been reported for starch recovery.[86]

The isolation through extraction from agro-food wastes of specific compounds, like fatty, organic, or amino acids, or the fermentation of the biomass for obtaining specific monomers is also interesting for the production of new biopolymers. Indeed, these compounds can be the base for biopolymer synthesis, like polylactic acic (PLA) and polyesteramides (PEAs). PEAs are innovative synthetic bio-based and biodegradable polymers, not as well-known as PLA or PHAs. PEAs constitute a promising family of biodegradable materials since they combine a degradable character, afforded by hydrolysable ester groups in the backbone, with relatively good thermal and mechanical properties due to the strong intermolecular hydrogen bonding interactions between their amide groups.[87]

As mentioned before, plant wastes often contain residual amounts of different bioactive compounds (*e.g.*, glucosinolates, phenolic acids, and flavonoids) characterized by remarkable health-promoting properties with strong immunomodulatory, antimicrobial, antioxidant, and anti-inflammatory actions.[88] These bioactive compounds need to be recovered from the waste source through feasible and efficient extraction processes. The most common and easily implementable extraction process is conventional solid–liquid extraction. The choice of the solvents is crucial to maximize the extraction of the target compounds while minimizing co-extraction of undesired components, together with the proper set of the operating conditions of the process (*e.g.*, temperature, time, solid–liquid ratio, *etc.*) depending on the target bioactive and the specific matrix.[89] The main disadvantage of this kind of process is the requirement of expensive and potentially hazardous organic solvents. Therefore, different, potentially greener extraction techniques (*e.g.*, microwave-and ultrasounds-assisted extraction, deep eutectic solvents, *etc.*) are under investigation.[90,91] The release of bioactive compounds from vegetables can be enhanced using electric fields such as pulsed electric and moderate electric fields[92] or using enzyme preparations that are environmentally friendly technologies.[93] However, the main limitation for the application of enzymes in industrial extraction processes is their relatively high cost.[93,94]

Apart from the extraction of isolated compounds from plant biomass and their transformation in bioplastics, the latter can also be obtained by the direct processing of the entire agrowaste biomass either by biotechnological or by chemical routes. Regarding, biotechnological transformation, biopolymers can be directly produced through microbial fermentation starting from plants and plant wastes, with most known examples the polyhydroxyalkanoates (PHAs) and the bacterial cellulose (BC). For example, Vega-Castro *et al.* obtained PHA from pineapple peel waste using *Ralsthonia eutropha.*[95] Before the fermentation process, pineapple peels were hydrolyzed using sulfuric acid (2% v/v). Then, fermentation was conducted inoculating the specific culture. Other authors have also used waste streams as carbon sources for bacterial PHA production, including whey,[96] spent coffee grounds,[97] grass biomass,[98] and fruit waste.[99] Similarly, BC is produced by some bacteria, being the ones from the genus *Komagataeibacter* the most used for research and food applications, since they produce BC with high purity and yield.[100] The main difference among these two biopolymers is that BC is synthetized extracellularly, while PHAs are produced intracellularly in the form of granules. Details on the methods of synthesis and properties of bio-based polyesters, polyesteramides and BC are not part of the scope of this manuscript and for more information about them the reader can refer to other recent publications.[87,100–102]

Regarding chemical transformation, the entire plant biomass from agrowastes, when treated with different acids, such as hydrochloric,[12] formic[103] and acetic,[104] but also with alkali solutions such as ammonium hydroxide,[105] results in deconstruction of its plant cell structure and hydrolysis of its components, and eventually, in solutions or dispersions of partially hydrolyzed natural polymers and phytochemicals. The resulting solutions and dispersions, after casting or spraying and solvent evaporation, can reassemble into stand-alone, compact, self-assembled composites, but sometimes, the hydrolyzed vegetable biomass needs to be combined with other additives or natural polymers or biopolymers to obtain consistent materials suitable for food packaging. For instance, when the amount of starch present in the vegetable waste is high enough, the materials obtained are fragile and need a plasticizer.[106] Besides, when the fiber content is high, the biocomposites can be blended with other amorphous polymers acting as binding agents.[66]

The sections 3 and 4 of this review that follow, present protective films and coatings respectively, which contain partially or totally biomass from agrowastes, and are developed for food protection through combinations of the above described processes.

3 Films for food packaging from agro-food waste

In this section, we present examples of agrowaste biomasses transformed into biocomposite films, either as additives or through chemical processing, intended for food packaging. The mechanical, barrier, antioxidant, and antimicrobial properties of the obtained films are discussed with respect to their potential in food protection. A summary of the main results discussed below, is shown in Table 1.

Agrowastes discussed in this section include both lignocellulosic biomass such as husks, shells, stems and straw, and non lignocellulosic biomass like pomace, seeds, fruit puree and peels. There are also considered formulations prepared with the addition of extracted phytochemicals such as EOs, waxes, and polyphenols.

3.1 Films with suitable mechanical and barrier properties

Since the biopolymers present in plant biomass are commonly hydrophilic, with shorter chain lengths and have more complex structures than their petroleum-based counterparts, the mechanical (Fig. 3A) and water vapor barrier properties of

Table 1 Composition and principal properties of biocomposite films obtained from agrowastes and agro-food byproducts and their properties related to food packaging

			Mechanical properties				Antioxidant activity				Barrier properties		Antimicrobial activity	
Agro waste	Other components	Solvent/ method	TS (MPa)	Eb (%)	YM (MPa)	Moisture content (%)	TPC	DPPH	ABTS	FRAP	WVP ($\times10^{-10}$ g per P.a.s.m)	O_2P ($\times10^{-9}$ cm^3 per m.d.Pa)	Inhibition area (mm^2)	Ref.
Blueberry pomace fiber	Gelatin waste and glycerol	Distilled water/ casting	1.51 ± 0.06	86.33 ± 5.13	735.83 ± 3.43	21.82 ± 1.19	Not assessed	Not assessed	Not assessed	Not assessed	2.4 ± 0.11	Not assessed	Not assessed	de Moraes Crizel *et al.*, 2016[112]
Grape skin pomace	Chitosan and glycerol	Acetic acid aqueous solution/ casting	Not assessed	Not assessed	Not assessed	17.05 ± 0.46	~2 mg GAE per g film	Not assessed	Not assessed	5 mg AAE per g film	9.3 ± 0.23	~1.2	Not assessed	Kurek *et al.*, 2019[132]
Olive pomace flour	Chitosan and glycerol	Acetic acid aqueous solution/ casting	2.89 ± 0.06	13.31 ± 0.77	12.39 ± 0.39	16.47 ± 0.87	Not assessed	2.48 ± 0.2 μM Trolox per g film	Not assessed	7.84 ± 0.2 μmol $FeSO_4{\cdot}7H_2O$	6.19 ± 0.38	Not assessed	Not assessed	de Moraes Crizel *et al.*, 2018[133]
Olive pomace microparticles	Chitosan and glycerol	Acetic acid aqueous solution/ casting	6.51 ± 0.02	20.93 ± 0.69	16.28 ± 0.83	15.04 ± 0.28	Not assessed	2.73 ± 0.18 μM Trolox per g film	Not assessed	11.28 ± 0.23 μmol $FeSO_4{\cdot}7H_2O$	3.02 ± 0.55	Not assessed	Not assessed	de Moraes Crizel *et al.*, 2018[133]
Avocado peel and seed	Pectin and polyglycerol-3	Acetic acid aqueous solution/ casting	17.9 ± 2.7	16.8 ± 6.1	341.7 ± 46.3	Not assessed	Not assessed	3.4 ± 0.2 μmof Trolox per g dried sample	Not assessed	Not assessed	18.0 ± 0.6	22.5 ± 1.5	Not assessed	Merino, Bertolacci, *et al.*, 2021[66]
Potato peel	Polyglycerol-3	Acetic acid aqueous solution/ casting	12.7 ± 1.5	18.4 ± 4.3	432.1 ± 86.4	16.4 ± 3.2	Not assessed	Not assessed	Not assessed	Not assessed	3.1 ± 0.3	5.5×10^3	Not assessed	Merino, Paul, *et al.*, 2021[106]
Coffee extract and husk fibers	Glycerol and corn starch	Not applicable/ melt blending and compression molding	11.2 ± 1.2	12.9 ± 2.6	386 ± 25	Not assessed	Not assessed	79.1 ± 6.6 mg film per g DPPH	Not assessed	Not assessed	38.8 ± 4.72	2.07 ± 0.17	Not assessed	Collazo-Bigliardi *et al.*, 2019[110]
Rice extract and husk fibers	Glycerol and corn starch	Not applicable/ melt blending and compression molding	12.1 ± 0.8	16.4 ± 3.6	541 ± 16	Not assessed	Not assessed	114.0 ± 0.7 mg film per g DPPH	Not assessed	Not assessed	33.8 ± 1.11	1.81 ± 0.77	Not assessed	Collazo-Bigliardi *et al.*, 2019[110]
Wheat starch and Oat CNCs	Glycerol	Distilled water/ casting	0.7 ± 0.33	32.8 ± 0.81	56.58 ± 9.06	16.08 ± 1.5	Not assessed	Not assessed	Not assessed	Not assessed	0.28 ± 0.01	Not assessed	Not assessed	Bruni *et al.*, 2020[116]
Phosphorylated wheat starch and Oat CNCs	Glycerol	Distilled water/ casting	3.52 ± 0.14	50.20 ± 2.44	24.3 ± 1.55	21.26 ± 0.71	Not assessed	Not assessed	Not assessed	Not assessed	0.13 ± 0.01	Not assessed	Not assessed	Bruni *et al.*, 2020[116]
Sugar palm starch and NCC	Glycerol and sorbitol	Distilled water/ casting	11.47 ± 0.1	24.42 ± 0.2	178.88 ± 0.2	12.70 ± 0.38	Not assessed	Not assessed	Not assessed	Not assessed	8.17 ± 0.05	Not assessed	Not assessed	Ilyas *et al.*, 2018[117]
Banana flour pomace	Glycerol, and KMS	Distilled water/ casting	1.65 ± 0.03	21.26 ± 3.28	Not assessed	Not assessed	Not assessed	Not assessed	Not assessed	Not assessed	0.16 ± 0.06	Not assessed	Not assessed	Jirukkakul, 2016[140]
Banana puree	Glycerol and KMS	Distilled water/ casting	1.45 ± 0.05	17.73 ± 1.97	Not assessed	Not assessed	Not assessed	Not assessed	Not assessed	Not assessed	0.65 ± 0.035	Not assessed	Not assessed	Jirukkakul, 2016[140]

Table 1 *(Contd.)*

Agro waste	Other components	Solvent/ method	Mechanical properties			Moisture content (%)	Antioxidant activity				Barrier properties		Antimicrobial activity	Ref.
			TS (MPa)	Eb (%)	YM (MPa)		TPC	DPPH	ABTS	FRAP	WVP ($\times10^{-10}$ g per P.a.s.m)	O_2P ($\times10^{-9}$ cm^3 per m.d.Pa)	Inhibition area (mm^2)	
Carrot puree	—	Hydrochloric acid in distilled water/ casting	38 ± 5	~6 ± 1	1300 ± 200	Not assessed	Not assessed	Not assessed	Not assessed	Not assessed	Not assessed	~90 000 ± 5000	Not assessed	Perotto *et al.*, 2018[12]
Papaya puree	De-fated soy protein, soy protein starch, glycerol and gelatin	Distilled water/ casting	68.0 ± 0.06	22.38 ± 0.06	Not assessed	Not assessed	Not assessed	Not assessed	Not assessed	Not assessed	15.4 ± 1.36	7.84 ± 0.07	Not assessed	Tulamandi *et al.*, 2016[123]
Lime peel pectin	Glycerol	Ethanol and distilled water/ casting	14 ± 1.82	4.6 ± 1.17	441.08 ± 43.17	21.92 ± 3.25	75.15 ± 2.67 (mg GAE per g film)	40.22 ± 0.44 μM Trolox per g film	532.04 ± 472 μM Trolox per g film	Not assessed	2.12 ± 0.04	7.84 ± 0.07	Not assessed	Rodsamran and Sothornvit, 2019[131]
Pomelo peel	Glycerol, sodium alginate and tea polyphenols	Distilled water/ casting	61.43 ± 0.15	10.74 ± 0.15	Not assessed	Not assessed	26.63 ± 0.25 μM Trolox per g film	51.72 ± 0.02% RSA	Not assessed	Not assessed	2.02 ± 0.02	Not assessed	*E. coli*: 13.65 ± 0.07 mm, *S. aureus*: 14.71 ± 0.17 mm	Wu *et al.*, 2019[127]
Mango peel	Glycerol	Citrate buffer solution (pH = 4.5)/casting	Not assessed	Not assessed	Not assessed	3.11 ± 0.84	14.67 ± 3.57 GAE per g film	51.90 ± 3.57% RSA	Not assessed	Not assessed	0.88 ± 0.02	Not assessed	Not assessed	Torres-León *et al.*, 2018[125]
Mango peel and mango seed extract	Glycerol	Citrate buffer solution (pH = 4.5)/casting	Not assessed	Not assessed	Not assessed	4.14 ± 1.3	44.42 ± 4.82 mg GAE per g film	63.55 ± 3.62% RSA	Not assessed	Not assessed	1 ± 0	Not assessed	Not assessed	Torres-León *et al.*, 2018[125]

Abbreviations: TS, Tensile strength; Eb, Elongation at break; YM, Young's modulus; TPC, total polyphenol content; WVP, water vapor permeability; O_2P, oxygen permeability; GAE, gallic acid equivalents; RSA, radical scavenging activity and AAE, ascorbic acid equivalents.

the obtained films are usually inferior.[106] Therefore, many approaches have been developed so far to overcome these drawbacks and offer efficient, apart from sustainable, films suitable for food transportation and protection.

A first approach, is the addition of lignocellulosic biomass to natural polymers. Lignocellulosic biomass in addition to being low-cost, and to show high strength, low density, biodegradability, availability, and renewability, can also effectively improve mechanical and barrier properties of natural polymers when added at relatively small percentages.[107,108] For example, the incorporation of lignocellulosic biomass has been demonstrated to improve the mechanical behavior of some starch-based composites.[109] Rice and coffee husks were added separately at 5 wt% in a corn starch matrix plasticized with 30 wt% of glycerol. The composite materials were prepared by melt blending followed by compression molding, and mechanical characterization demonstrated a 100% improvement on the tensile strength (TS) with respect to the control starch substrate (5.2 ± 1.6 MPa).[110] Similarly, lignocellulosic fibers from corn stalks, husks, and cobs were added to a starch water solution at concentrations ranging from 5 to 20 wt%. The films obtained by casting showed increases in TS and Young's modulus (YM) in the case of 5 and 10 wt% fiber content.[109]

However, lignocellulosic fiber-reinforced composites often present different manufacturing defects associated with the poor dispersion and big size of the fibers, as well as the lack of compatibility between them and the matrix, which usually leads to fibers' agglomeration and negatively affects the overall mechanical properties.[111] For example, de Moraes Crizel *et al.*, has prepared gelatin-blueberry fiber composite films by casting. The incorporation of 15 wt% of blueberry fibers into gelatin, reduced the TS of the matrix by 40% due to the fibers' agglomeration, observed by scanning electron microscopy at the cross-section surface.[112] Nevertheless, the chemical modification either of the matrix or of the additive biomass, as well as the use of compatibilizers, were able to improve the cohesion between the components. In particular, the butyl methacrylate acid has been employed to enhance the compatibility between coconut shells and regenerated cellulose biocomposites prepared by casting. The regenerated cellulose with 3 wt% of butyl methacrylate acid-treated and untreated coconut shells exhibited a TS of 62 and 55 MPa, respectively. Above this concentration, the strength was reduced due to low-dispersion and the agglomeration of coconut shell fibers.[113]

Another strategy to avoid fillers agglomeration and composites' defects is to use purified cellulose nanocrystals (CNCs) at even lower concentrations. CNCs have received growing interest as polymers' reinforcing agents in recent years, since their uniform distribution into a polymeric matrix improves its mechanical performance and barrier properties.[114] In the work of Kargarzadeh *et al.*,[115] the authors prepared composites of cassava starch with untreated rice husk fibers, bleached rice husk fibers, and rice husk-derived CNCs (Fig. 3B) by casting. Results showed that untreated fibers weakened the TS, bleached fibers improved it by 12%, while 6 wt% of CNCs produced an increase of 52% in the TS.[115] The authors attributed these results to the different dimensions of the fibers and the lack of cohesion between the untreated fibers and the matrix. Bruni *et al.* have reported the preparation of biocomposites, by adding CNCs derived from different plant sources (rice, oat, and eucalyptus) into a phosphorylated wheat starch matrix, by the method of solution casting.[116] Results indicated that the incorporation of the CNCs resulted in an improvement of the water-resistance and mechanical properties of the materials.[116] In the same way, Ilyas *et al.* have prepared and analyzed the mechanical properties of plasticized sugar palm starch-sugar palm CNCs composites obtained by casting. They found an enhancement in the thermoplastic starch films' mechanical resistance showing the highest TS at 0.5 wt% of CNCs, the double of the sugar palm starch films.[117]

Besides their application as reinforcement agents, CNCs have demonstrated to improve the barrier properties of biocomposites when they are well-dispersed in the polymer matrix.[114] This happens because the incorporation of CNCs provides reduced gas diffusion by increasing the tortuosity path through the materials.[114] For example, in over-ripe papaya puree films obtained by casting, the water vapor diffusion was reduced by 50% with the incorporation of 0.2 wt% of cellulose nanofibers (CNFs), while an improvement in the TS of the neat puree film was also observed.[118] Similarly, the water vapor permeability (WVP) of sugar palm starch films obtained by casting decreased up to 18% when 1 wt% of CNCs was loaded.[117]

Alternatively, the addition of lignin as filler in composites is also being considered as strategy for mechanical and barrier properties improvement. For instance, soy protein isolate films with 30–40% of sulfonated lignin prepared by melt blending followed by compression molding, demonstrated the simultaneous enhancement of the TS and YM of the pure soy protein films together with a decrease in the material's water absorption.[119] Interestingly, Tedeschi *et al.* combined different proportions of cellulose, commercial Kraft lignin, and xylan to fabricate multifunctional lignin-based bioplastics by casting method after treating materials in different concentrations under acidic media. Results showed that lignin increased the stiffness and the oxygen and water transmission barrier of the wood-like biocomposites (Fig. 3C), exhibiting barrier and mechanical properties comparable to petroleum-based and commercial polymers.[67]

Another strategy used for improving plant-based films' barrier properties includes the addition of small functional phytochemical substances, such as lipophilic EOs, into a biopolymer matrix. It has been demonstrated that they enhance water resistance and provide films with antimicrobial activity.[120] For example, sunflower seed oil substantially affected the water-resistance properties when incorporated into mung bean starch-guar gum films prepared by casting.[121] The WVP of this film with 2 wt% of sunflower oil showed a decrease of 30% on the WVP with respect to the film without oil. Similarly, improved water resistance and moisture barrier properties were reported when 50 wt% of apricot kernel EO was incorporated into chitosan films obtained by casting.[122]

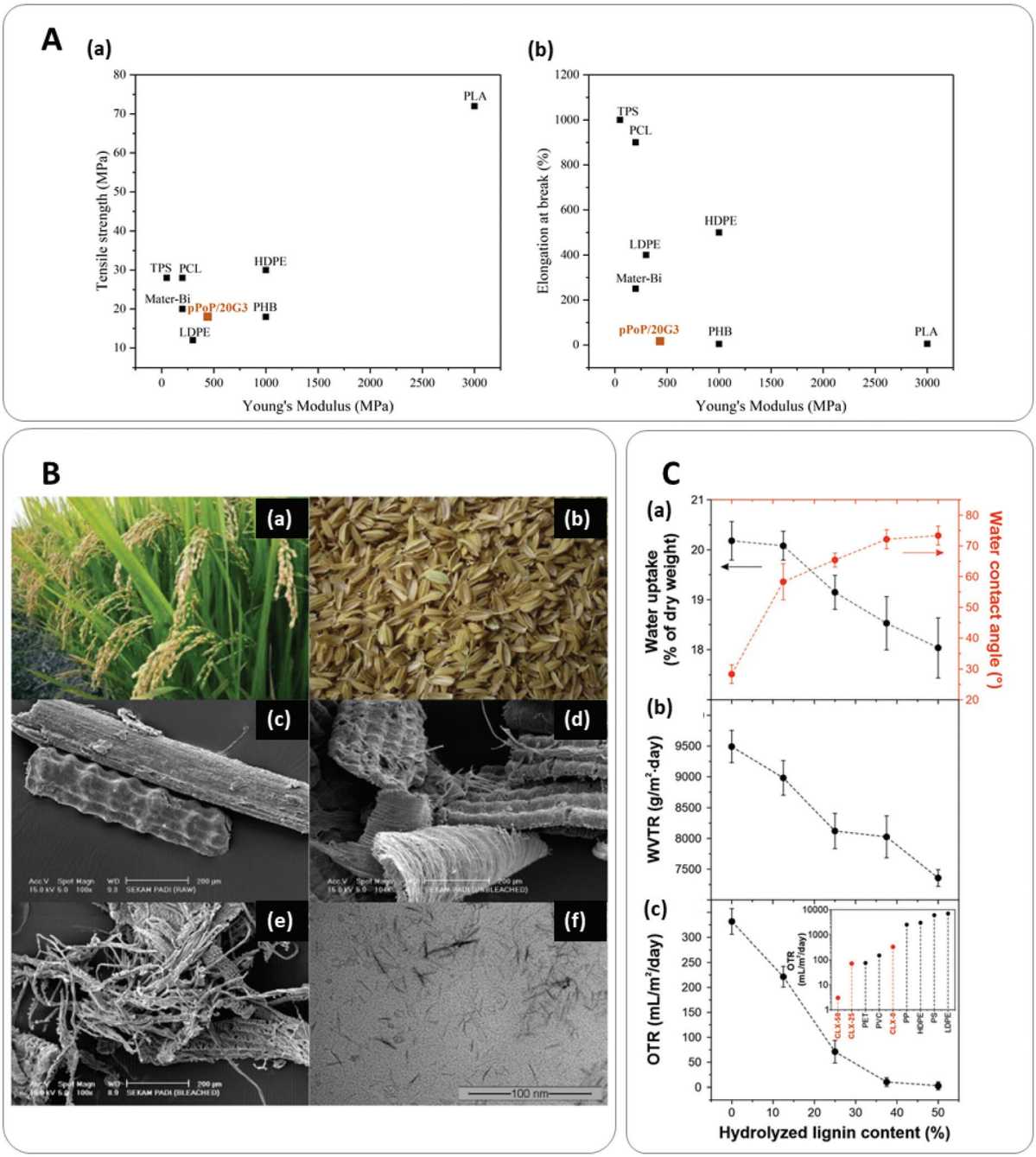

Fig. 3 Bioplastics with suitable mechanical and barrier properties. (A) Comparison of mechanical properties of potato peel bioplastic (dark orange square) with the mechanical properties of the materials commonly used for food packaging (black squares). (a) Plot of the tensile strength (MPa) *vs.* Young's modulus (MPa), and (b) Elongation at break (%) *vs.* Young's modulus (MPa). Reprinted from D. Merino, U. C. Paul and A. Athanassiou, Bio-based plastic films prepared from potato peels using mild acid hydrolysis followed by plasticization with a polyglycerol, *Food Packag. Shelf Life*, 29, 100707, Copyright (2021), with permission from Elsevier. (B) Photographs of (a) rice paddy, (b) rice husks and SEM images of (c) raw fiber, (d) alkali-treated fiber, and (e) bleached fiber and (f) TEM image of rice husk-derived CNCs. Reprinted from H. Kargarzadeh, N. Johar and I. Ahmad, Starch biocomposite film reinforced by multiscale rice husk fiber, *Compos. Sci. Technol.*, 151, 147–155, Copyright (2017), with permission from Elsevier. (C) (a) Water uptake and water contact angle, (b) water vapor transmission rate (WVTR), and (c) oxygen transmission rate (OTR) values, for lignin-based bioplastics as a function of the hydrolyzed lignin content. Inset of (c) shows OTR values of the natural composite with lignin (CLX) in comparison to common petroleum-based plastics for packaging. Reprinted from G. Tedeschi, S. Guzman-Puyol, L. Ceseracciu, U. C. Paul, P. Picone, M. Di Carlo, ... and J. A. Heredia-Guerrero, Multifunctional bioplastics inspired by wood composition: effect of hydrolyzed lignin addition to xylan–cellulose matrices, *Biomacromolecules*, 21(2), 910–920, Copyright (2020), with permission from ACS.

The mixture between the hydrophilic carbohydrates with the hydrophobic EOs creates an emulsion system. The emulsion stability and dispersion of the oil droplets have an essential effect on the material's properties. The average size of oil droplets tends to grow due to the coalescence effect limiting the material's efficiency against water vapor and pathogens growth prevention.[120,123] In the work of Li *et al.*, the octenylsuccination of sweet potato starch enhanced the dispersion of the oregano EO (1.5 wt%), reducing in 60% the water vapor permeability of the casted biocomposites films respect to the non-grafted sample with the same content of oregano EO.[120] Interestingly, citrus peels, which are rich in cuticular waxes, EOs, and terpenes, provide peel waste-based films with high moisture barrier properties.[124] For example, films obtained by casting method based on mango peel presented a WVP of 0.88×10^{-10} g m^{-1} s^{-1} Pa^{-1}, which is inferior to the permeability observed for materials prepared from other vegetable wastes,[125] but still superior to the one of PE (5.5×10^{-13} g m^{-1} s^{-1} Pa^{-1}),[126] for example.

Another strategy used to improve polysaccharide-based biocomposite films' barrier properties is to combine them with proteins to form blends or bilayers.[75] Proteins show significate advantages over the polysaccharides discussed in the previous paragraphs, associated with their structure, and in particular with the wide variety of amino acids (the monomers of the proteins) that comprises them. Proteins rich in non-polar and hydrophobic amino acids (*e.g.* glycine, alanine, proline, valine) such as zein and kerfirin are significantly more water resistant than the polysaccharide biopolymers, while proteins that can inherently crosslink, like wheat gluten proteins, could create strong and elastomeric materials. However, these vegetable proteins are produced in significantly smaller volumes compared to the lignocellulosic components or to the proteins from other sectors such as collagen or keratin. This difference in available volumes of raw materials, makes it difficult to realistically substitute a significant percentage of plastic with protein-derived materials from vegetables. Nevertheless, their unique properties could allow them to be used for high added value-applications, like water resistant coatings of more readily available substrates or as barrier films in multilayer bio-based packaging. For instance, soy protein has been used to improve the WVP of many polysaccharide biopolymers composites. Tulamandi *et al.*, reported that gelatin and defatted soy protein in different proportions, were incorporated into composites made mainly by papaya puree to improve their barrier properties and water resistance. Films produced by casting with 3 wt% of gelatin and 4 wt% of defatted soy protein decreased the water vapor permeability by 34% with respect to the control film.[123]

3.2 Films with antimicrobial and antioxidant properties

The large amount of bioactive compounds present in the agro-waste biomass may provide the bioplastics derived from it with antioxidant and antimicrobial activities.[127,128]

The most widely explored strategy to prevent the risk of pathogen growth is to incorporate safe antimicrobial additives into the films. For that, organic acids, chitosan biopolymer, nisin peptide, plant extracts, and EOs are usually the options of choice.[61,129] For example, the volatile terpenoids and phenolic compounds of different EOs demonstrated to inhibit the microbial activity of *E. coli*, *S. enterica*, and *L. monocytogenes* by both direct and indirect contact (vapor diffusion) when incorporated into an apple peel film, developed upon drop casting from water-based solutions. Remarkable differences were observed between the two methods, indicating that such EOs' vapor phases led to more significant bacterial inhibitory effects.[130]

On the other hand, non-lignocellulosic biomass or its by-products such as fruit peels and pomace extracts have been widely selected as ingredients in active food packaging. For instance, in the work of Nur Hanani *et al.* examples of the excellent antimicrobial and antioxidant properties of plant peels are delivered. These authors have incorporated the peel powders of pomegranate, papaya, and jackfruit into a gelatin matrix, in order to avoid the growth of the pathogens in a gelatin-polyethylene bilayer material.[128] The fruit peel powders were incorporated into fish gelatin film-forming solutions and were directly casted on a polyethylene layer. Among them, pomegranate peel powder provided excellent antimicrobial properties against different Gram-positive and Gram-negative bacteria. Simultaneously, papaya peel powder embedded in the bilayer exhibited excellent antioxidant properties, reaching 78% of 2,2-diphenyl-1-picrylhydrazyl free radical (DPPH) inhibition, comparable to a maximum of 76% of inhibition obtained by the same bilayer loaded with chitosan powder.[128] Another example of the great antioxidant capacity of fruit peel was reported by Rodsamran and Sothornvit, who incorporated a 10 wt% ethanolic extract of lime peel into lime peel pectin films obtained by casting and enhanced its antioxidant capacity more than 11 times against 2,2′-azino-bis(3-ethylbenzothiazoline-6-sulfonic acid radical (ABTS) dissolved in water.[131] Similarly, bioactive films prepared by solution casting method made of pomelo peel flour and tea polyphenols in different concentrations (5, 10, 15, and 20 wt%) prevented the development of both Gram-positive and Gram-negative bacteria, as well as reduced the lipid oxidation of soybean oil samples placed in a glass vial sealed on the top with the film, limiting the migration of oxygen gas molecules.[127]

Similarly, fruit pomace was also reported to provide active properties to bioplastics. For example, the fibers and the ethanolic extract of blueberry pomace obtained from juice blueberry processing were isolated and added separately to a gelatin-based matrix to develop active and environmentally-friendly packaging films by the casting technique.[112] As expected, the addition of pomace by-products demonstrated excellent antioxidant properties avoiding the lipid oxidation of the packed sunflower oil. For these tests, gelatin films with a fiber concentration of 0.15 g mL^{-1} were sealed to form packages containing 7 g of sunflower oil, and its oxidation, represented as peroxide value (PV) (mEq O_2 per kg oil), was monitored during 13 days using a transparent plastic bag as control. Interestingly, while the oxidation of sunflower oil

increased up to 70 mEq O_2 per kg after 13 days of storage in the control, the gelatin/pomace based package inhibited by 100% the oil oxidation.[112] Kurek *et al.* have also reported antioxidant properties in chitosan and carboxymethyl cellulose films prepared by casting by adding blueberry and red grape skin pomace extracts in 1, 2, and 4 wt%. In this case, antioxidant activity was measured by Ferric Reducing Antioxidant Power (FRAP) assay, which evaluates the scavenging capacity of polyphenols present in extracts against a radical reagent. Results showed that the antioxidant response was proportional to the concentration of extract and that it was higher when grape skin pomace extract was used. Chitosan films with 4 wt% of the grape skin pomace extract exhibited seven times higher antioxidant activity (mg ascorbic equivalents per g film) than chitosan films with blueberry pomace extract.[132] Similarly, de Moraes Crizel *et al.* have demonstrated that olive pomace incorporated into chitosan films prepared by casting protects walnuts from oxidation when packed in this material. Protected samples showed inferior PV, dienes, and trienes in walnuts, after 31 days of storage, significantly differing ($p < 0.05$) from the ones non-packaged or packed in a chitosan film or a commercial plastic packaging.[133]

Furthermore, lignocellulosic biomass was also reported to provide antioxidant properties to bioplastics. For instance, antioxidant bioplastics were reported for thermoplastic corn starch composites prepared upon melt blending and compression molding with rice and coffee husks,[110] and for pectin composites films obtained by casting with avocado peels,[66] measured this property in all cases against the DPPH radical.

3.3 Films as indicators or sensors of food spoilage

A new trend followed by researchers in the area of intelligent food packaging development uses natural dyes to inform consumers about the quality of food during storage. Phytochemical molecules such as curcumin, alizarin and anthocyanins are sensitive to changes in pH, and respond by a color change upon pH change, that allows consumers to identify the state of freshness of food by naked eye and in real time.[134]

The integration of the bioactive compounds as high-added value compounds in the formulation of bioplastic films can also be exploited to develop additional functionalities, such as radical scavenging or as protection against oxidant agents.[135] These compounds are often encapsulated to avoid their degradation by oxidation or by the high temperatures commonly used during industrial processing of polymeric materials such as extrusion and blow-molding.[136] Several authors have reported encapsulation methods to incorporate anthocyanin into a biopolymer matrix to obtain active colorimetric pH-sensitive films.[136,137] For example, Moazami Goodarzi *et al.* have reported the development of a starch-filter paper-based film with immobilized anthocyanin of black carrot by immersion of the filter paper into a starch solution to monitor the spoilage of milk in a range of 24 h. During the storage of milk, microbial activity leads to pH changes that can be easily detectable using these innovative bio-based films (Fig. 4A).[138] A different work reported black chokeberry pomace extract encapsulation into a chitosan matrix and the realization of films by casting, demonstrating pH-responsive color change: red color at acidic media (pH 1–3) and blue above pH 7 (Fig. 4B).[137] In another work, the flower extract of Jamaica (Hibiscus sadbariffa) was incorporated into a nanoclay and added as filler into a thermoplastic corn-starch matrix by extrusion. Results showed that in that case, the incorporation of the extract in the nanoclay reduced the pH-sensibility of the anthocyanin due to the lack of permeability of samples limiting its use as an indicator.[136,137]

In most cases, the response to changes in pH is evaluated in aqueous media, not entirely appropriate to simulate realistic applications and generally obtaining a slow and non-perceptible optical response at all pH values. The response time is associated to the compact structure of the films or, as mentioned above, to the fact that these substances are usually encapsulated in other matrices to improve their chemical stability. Zia *et al.*[139] have recently managed to overcome this limitation through the development of porous indicators loaded with anthocyanins, which allowed to significantly improve the response time in environments of different pHs (Fig. 4C). To do this, they used anthocyanins extracted from red cabbage and loaded them on freeze-dried porous networks of polyvinylpyrrolidone (PVP) and MCC. Although the PVP polymer is not derived from biomass, this work demonstrates that anthocyanin-based porous systems were capable of rapidly detecting the presence of both acidic and basic vapors in a few seconds and that they can be reused for at least 15 times. These sensors open up the possibility of developing smart packaging for food, although work still needs to be done on the development of completely bio-based systems, in accordance to the principles of green chemistry.

4 Edible active food coatings from agrofood waste

An edible coating is a semi-permeable layer applied directly on food that becomes an integral part of the food product.[141,142] The final aim of food coatings is to extend the food shelf-life by reducing the exchange of moisture, O_2, CO_2, lipids, and volatile molecules between the food and the surrounding environment. As mentioned above for food packaging films, coatings derived from vegetable and fruit by-products also contain bioactive molecules with antioxidant and antimicrobial properties, which can improve the preservation of perishable functional foods.[142,143]

The requirements for a coating material should be linked to the coated food physicochemical properties, which change enormously between the various food types (vegetables, fruits, fish and meat). For example, the high content of lipids and proteins in meats and seafood makes these foods more susceptible to microorganisms' growth. Therefore, their coatings are expected to present a vital microorganism inhibition capacity. On the other hand, coatings for food such as fruits and veg-

Fig. 4 Natural pH indicators. (A) Color changes for starch-paper films with carrot anthocyanins at different pH values (pH 2–11). Reprinted from M. M. Goodarzi, M. Moradi, H. Tajik, M. Forough, P. Ezati and B. Kuswandi, Development of an easy-to-use colorimetric pH label with starch and carrot anthocyanins for milk shelf life assessment, *Int. J. Biol. Macromol.*, 153, 240–247, Copyright (2020), with permission from Elsevier. (B) Color changes for chitosan films with different contents of black chokeberry pomace extract (AEX). Reprinted from K. Halász and L. Csóka, Black chokeberry (*Aronia melanocarpa*) pomace extract immobilized in chitosan for colorimetric pH indicator film application, *Food Packag. Shelf Life*, 16, 185–193, Copyright (2018), with permission from Elsevier. (C) (a) Red cabbage anthocyanins (RCAs) solution response upon pH changes. (b) The PVA-PVP foam with MCC (thickness: 3.0 mm ± 0.2 mm, diameter: 14 mm) after dipping in solutions of different pH (in each case 10 ml for 3 min). Reprinted from J. Zia, G. Mancini, M. Bustreo, A. Zych, R. Donno, A. Athanassiou and D. Fragouli, Porous pH natural indicators for acidic and basic vapor sensing, *Chem. Eng. J.*, 403, 126373, Copyright (2021), with permission from Elsevier.

etables should be focused on slowing down the respiration rate and thus, retarding their ripening.[141] Additionally, edible coatings should be tasteless and should not modify the sensory characteristics of the food.[1,75] Advances made in the valorization of vegetable and fruit wastes to fulfill these requirements and a review of the latest publications in this field are summarized in Table 2 and included in the following subsections.

4.1 Coatings reducing fruits and vegetable respiration rate

Fruits and vegetables are living organisms, which means that many biochemical processes are still ongoing after harvesting, with important consequences on their physical appearance and nutritional quality. Respiration is a metabolic process linked to the consumption of oxygen (O_2) and the release of carbon dioxide (CO_2) and differs from the process of ripening. However, high respiration rates correspond to rapid ripening and senescence, resulting in low durability and a more perishable product. Ncama *et al.* suggested that coatings' application limits the transpiration rate because they partially block the stoma of vegetables.[142] The respiration rate is usually evaluated by measuring the change in the concentration of headspace gas (CO_2 and O_2) when coated samples are placed in closed trays during the experiments for the determination of the

Table 2 Chemical composition and preservation features of coatings based on agrowaste

Agro waste	Other components	Solvent	Food coated	Respiration		Weight loss (%)	ΔFirmness (N)	ΔTexture	ΔLightness (L*)	ΔWhiteness index (WI)	ΔLipid oxidation (mg MDA per kg meat)	Antibacterial activity	Ref.
				Δ[O_2] (%)	Δ[CO_2] (%)								
Carrot puree	Citric acid	Distilled water	Fresh cut carrot	Not assessed	Not assessed	Coated: 0.8% after 12 days, Uncoated: 1.5% after 12 days	Coated: ↓40% after 12 days, Uncoated: ↓65% after 12 days	Not assessed	Not assessed	Coated: ↑7% after 12 days, Uncoated: ↑40% after 12 days	Not assessed	Not assessed	Wang *et al.*, 2015[157]
Margo kernel starch	Sorbitol and starch	Distilled water	Tomato fruit	Not assessed	Not assessed	Coated: 8% after 20 days, Uncoated: 12% after 20 days	Coated: ↓50% after 20 days, Uncoated: ↓90% after 20 days	Not assessed	Not assessed	Not assessed	Not assessed	Not assessed	Nawab, Alam, and Hasnain, 2017[171]
Pomegranate peel extract	Calcium sulfate	Distilled water	Cherry fruit	Not assessed	Coated: ↑133% after 45 days, Uncoated: ↑186% after 45 days	Coated: 28 after 45 days, Uncoated: 48 after 45 days	Coated: ↓28% after 45 days, Uncoated: ↓42% after 45 days	Not assessed	Coated: ↓1.6% after 45 days, Uncoated: ↓7.1% after 45 days	Not assessed	Not assessed	Not assessed	Parsa *et al.*, 2021[148]
Rice bran wax	Polysorbate-80	Distilled water	Tomato fruit	Coated: ↓25% after 122 h, Uncoated: ↓75% after 122 h	Not assessed	Coated: 10% after 27 days, Uncoated: 10% after 18 days	Coated: ↓62.5% after 27 days, Uncoated: ↓62.5% after 18 days	Not assessed	Not assessed	Not assessed	Not assessed	Not assessed	Abhirami, Modupalli, and Natarajan, 2020[144]
Sesame protein and mango puree	Maleic acid, glycerol, guar gum and $CaCl_2$	Distilled water	Fresh cut mango	Not assessed	Not assessed	Not assessed	Coated: ↓33% after 15 days, Uncoated: ↑10% after 15 days	Not assessed	Coated: ↓5.17% after 15 days, Uncoated: ↓21,12% after 15 days	Not assessed	Not assessed	Yes. Analyzed by total plate count.	Sharma *et al.*, 2019[152]
Sesame protein and mango puree	Succinic acid, glycerol, guar gum and $CaCl_2$	Distilled water	Fresh cut mango	Not assessed	Not assessed	Not assessed	Coated: ↓30% after 15 days, Uncoated: ↑10% after 15 days	Not assessed	Coated: ↓2.65% in 15 days, Uncoated: ↓21.12% after 15 days	Not assessed	Not assessed	Yes. Analyzed by total plate count.	Sharma *et al.*, 2019[152]
Sesame protein and mango puree	Citric acid, glycerol, guar gum and $CaCl_2$	Distilled water	Fresh cut mango	Not assessed	Not assessed	Not assessed	Coated: ↓30% after 15 days, Uncoated: ↑10% after 15 days	Not assessed	Coated: ↓3.50% after 15 days, Uncoated: ↓21.12% after 15 days	Not assessed	Not assessed	Yes. Analyzed by total plate count.	Sharma *et al.*, 2019[152]

Table 2 *(Contd.)*

Agro waste	Other components	Solvent	Food coated	Respiration		Weight loss (%)	ΔFirmness (N)	ΔTexture	ΔLightness (L*)	ΔWhiteness index (WI)	ΔLipid oxidation (mg MDA per kg meat)	Antibacterial activity	Ref.
				$\Delta[O_2]$ (%)	$\Delta[CO_2]$ (%)								
Sesame protein and pineapple juice extract	Glycerol, guar gum and $CaCl_2$	Distilled water	Fresh cut pineapple	Not assessed	Not assessed	Not assessed	Coated: ↓13% after 15 days, Uncoated: ↓25% after 15 days	Not assessed	Coated: ↓0.13% after 15 days, Uncoated: ↑3.78% after 15 days	Not assessed	Not assessed	Yes. Analyzed by total plate count.	Sharma *et al.*, 2018[153]
Sesame protein and pineapple juice extract	Maleic acid, glycerol, guar gum and $CaCl_2$	Distilled water	Fresh cut pineapple	Not assessed	Not assessed	Not assessed	Coated: ↓14% after 15 days, Uncoated: ↓25% after 15 days	Not assessed	Coated: ↓0.65% after 15 days, Uncoated: ↑3.78% after 15 days	Not assessed	Not assessed	Yes. Analyzed by total plate count.	Sharma *et al.*, 2018[153]
Sesame protein and pineapple juice extract	Succinic acid, glycerol, guar gum and $CaCl_2$	Distilled water	Fresh cut pineapple	Not assessed	Not assessed	Not assessed	Coated: ↓8% after 15 days, Uncoated: ↓25% after 15 days	Not assessed	Coated: ↑0.76% after 15 days, Uncoated: ↑3.78% after 15 days	Not assessed	Not assessed	Yes. Analyzed by total plate count.	Sharma *et al.*, 2018[153]
Sesame protein and pineapple juice extract	Citric acid, glycerol, guar gum and $CaCl_2$	Distilled water	Fresh cut pineapple	Not assessed	Not assessed	Not assessed	Coated: ↓6% after 15 days, Uncoated: ↓25% after 15 days	Not assessed	Coated: ↓0.76% after 15 days, Uncoated: ↑3.78% after 15 days	Not assessed	Not assessed	Yes. Analyzed by total plate count.	Sharma *et al.*, 2018[153]
Grapefruit seed extract	Carnauba wax, oregano essential oil and Tween 80.	Distilled water	Mandarins	Not assessed	Coated: ↓33% after 28 days, Uncoated: ↓10% after 28 days	Coated: 1% after 28 days, Uncoated: 2% after 28 days	Coated: ↓45% after28 days, Uncoated: ↓50% in 28 days	Not assessed	Coated: ↑9.22% after 21 days, Uncoated: ↑1.57% after 21 days	Not assessed	Not assessed	Yes. Against *P. Italicum*	Won and Min, 2018[154]
Sweet potato starch	Glycerol, Tween 80 and thyme essential oil	Distilled water	Shrimp	Not assessed	Not assessed	Not assessed	Not assessed	Coated: ↓6.08% after 8 days, Uncoated: ↓16.54% after 8 days	Not assessed	Not assessed	Coated: ↑<10% after 8 days, Uncoated: ↑100% after 8 days	Yes. Against aerobic bacteria	Alotaibi and Tahergorabi, 2018[159]
Plantago major seed mucilage	Citrus lemon essential oil	Distilled water	Buffalo meat	Not assessed	Not assessed	Not assessed	Not assessed	Coated: ↓14% after 10 days, Uncoated: ↓22% after 10 days	Coated: ↓7.5% after 10 days, Uncoated: ↓12.5% after 10 days	Not assessed	Not assessed	Yes. Measured against psychrotrophic bacteria, *E. coli*, *S. aureus* and Funghi	Noshad *et al.*, 2021[167]

Table 2 (Contd.)

Agro waste	Other components	Solvent	Food coated	Respiration		Weight loss (%)	ΔFirmness (N)	ΔTexture	ΔLightness (L^*)	ΔWhiteness index (WI)	ΔLipid oxidation (mg MDA per kg meat)	Antibacterial activity	Ref.
				Δ[O_2] (%)	Δ[CO_2] (%)								
Grape pomace	Sodium nitrite	Not applicable	Beef sausage	Not assessed	Not assessed	Not assessed	Not assessed	Not assessed	Not assessed	Not assessed	Coated: ↑3% after 30 days, Uncoated: ↑65% after 30 days	Yes. Measured by total viable count	Riazi *et al.*, 2016[172]

maximum storage time.[125,144] For example, the respiration rate of peaches coated by immersion during 10 minutes in a mango peel flour (MPF) and mango peel flour with the antioxidant extract of mango seed (MPFS) aqueous solution was evaluated and compared with peaches immersed in distilled water.[125] Results showed that MPF coating did not present significant differences with the control, but the MPFS coating slowed down the gas exchange up to 29% and 39% for CO_2 and O_2, respectively.[125] In the work of Panoth Abhirami *et al.*, the respiration rates of uncoated tomatoes (control) and dip-coated tomatoes treated with a rice bran wax coating emulsion prepared with polysorbate-80 in water were measured. Results indicated that the oxygen level underwent an important decline in uncoated tomatoes, while tomatoes coated with rice bran wax exhibited lower variation. At the end of the experiment (122 hours), uncoated tomatoes consumed three times more oxygen than tomatoes with rice bran wax.[144]

Interestingly, when the oxygen level decays below 3%, anaerobic respiration takes place. Anaerobiosis and fermentation processes lead to ethanol and acetaldehyde production, characterized by its unpleasant flavor.[145] Another ripening indicator is the release of ethylene from the fruit, especially in climacteric fruit such as apple, avocado, or tomato.[146,147] In Torres-León *et al.*, the ethylene emission was reduced by 64% for peach samples coated by immersion into mango peel flour solution prepared in citrate buffer solution (pH 4.5) after 8 days of storage.[125]

4.2 Coatings for texture preservation and reduced water transpiration of fruits and vegetables

Fruit softening is the major indicator of the shelf-life, and consequently, of the commercial value of the fruits and vegetables.[148] The loss of turgor in fruits is strongly related to the ripening, which triggers many physicochemical changes that provide to the fruit the characteristic texture, color, aroma, and taste upon maturation.[149] The problem appears when fruits overcome the maturation stage and overripe, leading to loss of firmness, senescence, and over-soften flesh. During ripening, starch degrades into smaller saccharides such as glucose, fructose, or sucrose, increasing the sweetness of the fruit, while the concentration of organic acids decreases, being the most critical losses those of maleic and citric acids. Thus, most fruits become softer during ripening due to the disaggregation of cell walls and starch degradation, which promote lower values of firmness and increase the transpiration of water.[149] The increase in water transpiration causes weight loss, a reliable parameter to determine plant degradation.[150] For example, uncoated tomatoes and tomatoes coated with a rice bran wax emulsion by dip-coating underwent a different rate of decay of firmness and weight during the storage. The application of the coating increased the shelf-life of the fruit, obtaining the same weight-loss (−10%) and firmness (−62.5%) values of the uncoated fruit but nine days later.[144]

It is well-known that reducing fruit and vegetable water loss prevents the softening of plant tissue. Several techniques have been developed with this aim, including the fruit dipping into

calcium salt solution to cross-link pectin present in the plant tissue and reinforce the cell wall's structural integrity.[148,151] For example, in the work of Parsa *et al.*, the application of a coating composed of 1 wt% calcium sulfate and 200 or 400 ppm pomegranate peel extract reduced the weight loss and firmness of sweet cherry fruits by 50% and 25%, respectively.[148]

The incorporation of lipophilic compounds, such as proteins, waxes, or EOs, into fruit coatings has significant effects on water transpiration and tissue firmness.[152,153] Hydrophobic sesame protein has been used to prepare a bilayer coating system to improve the shelf-life of mango and pineapple fruit.[152,153] The preservation properties, especially firmness, were improved when sesame protein was cross-linked with different organic acids (succinic, malic, and citric acid) before the coating application. The pineapple fruit was first immersed in a cross-linked sesame protein water solution, and then a second layer consisting of a water solution of mango puree and calcium chloride was applied. Coated pineapples exhibited up to 20% more firmness than uncoated fruit after 15 days of storage at 5 °C.[153] The weight loss associated with the water transpiration was reduced in Satsuma mandarin, after dip-coating during 30 seconds into an emulsion based on grapefruit seed extract and carnauba wax prepared with Tween 80 as emulsifier. After seven days of storage at 25 °C, the weight loss of coated mandarins was reduced by ~3 times in comparison to the uncoated mandarins.[154]

4.3 Coatings to avoid undesirable color changes in food

The enzymatic browning is one of the most important color reactions in nature that occurs to fruits, vegetables, and seafood, which harmfully affects the attractiveness and the consumption of these products.[155,156] The enzymatic browning starts due to the breaking down of the cell walls (cutting, peeling-off). Next, some environmental factors, such as temperature, pH, and oxygen concentration, induce the activation of Polyphenol oxidase (PPO) enzyme.[155,156] PPO enzyme catalyzes the first polymerization of phenols to produce quinones, which undergo further polymerization into dark pigments called melanoidin, represented in Fig. 5,[156] causing the brown coloration during fruit storage. Plant-based coatings, mainly composed of biomolecules with high polarity, may reduce non-polar molecules' transpiration like oxygen.

Moreover, vegetable and fruit wastes are rich in antioxidants, which avoid oxygen activity by scavenging.[141] In the work of Wang *et al.*, the PPO activity and total phenols were evaluated by spectrometry and monitored in fresh-cut carrots dip-coated during 5 minutes in a 30 wt% carrot puree-based

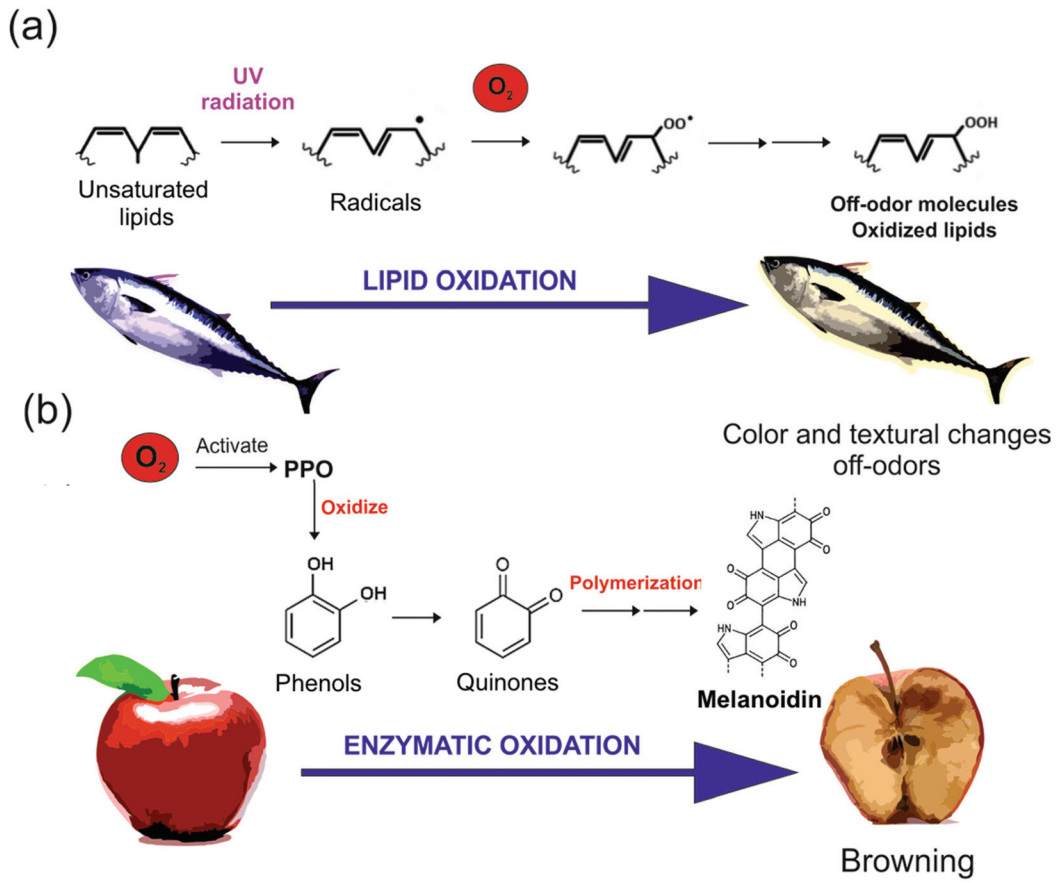

Fig. 5 Schematic representation of the process involved in (a) lipid oxidation and (b) enzymatic oxidation. PPO corresponds to the enzyme polyphenol oxidase.

water solution containing also 1 wt% corn starch, 0.5 wt% gelatin, 1.5 vol% glycerol, 1 wt% chitosan, and 1 vol% cinnamaldehyde. As expected, coated samples showed lower values of total polyphenols (~10 OD_{280} per g) and PPO activity (~160 U g^{-1}) compared to uncoated carrots (~22 OD_{280} per g and ~220 U g^{-1}, respectively).[157]

Besides the enzymatic oxidation, other factors also induce undesirable color changes in fruits, including cutting operation, surface dehydration, and non-enzymatic oxidation. The application of coatings on fruits and vegetables may prevent the tissue damage generated by these environmental conditions (changes in the temperature, pH, and relative humidity, for example).[141] Furthermore, the coating plays a fundamental role in preserving the natural color of the fruit, which is fundamental for its commercialization. The color changes can be evaluated during storage by colorimetric methods. The darkening of the fruit due to the undesirable browning process can be measured with the light (L*) values or with the whiteness index (WI) over the storage period[157] and the results found in the literature are summarized in Table 2.

4.4 Coatings with antimicrobial activity for fruits and vegetables

Vegetables and fruits present an outer protective waxy cuticle layer that avoids microbial growth. Besides, most of the fruits' characteristic acidity acts as a natural defense against the spoilage microbes. The manipulation and transportation of these foods usually result in the breakdown of this external layer that drives rapid colonization and development of several microorganisms.[158] Incorporating coatings may prevent external damage such as cracks and punctures while including antimicrobial agents into the coating can also limit microbial growth. EOs have demonstrated bactericide properties due to the hydrophobic constituents, capable of breaking down the microbial cell wall of the pathogens.[159] For instance, the incorporation of 0.5 wt% oregano EO into a coating based on grapefruit seed extract and carnauba wax was demonstrated to protect *Satsuma mandarin* against the fungus *Penicillium italicum.*[154] The diseases' effects were measured in coated and uncoated samples at two different temperatures (25 and 4 °C), showing less incidence at lower temperatures. The application of the previously described coating retarded the appearance of the symptoms caused by the fungi to 21 days, while uncoated samples manifested the disease after five days at 4 °C of storage temperature. Furthermore, the protective features of coatings derived from several vegetables and fruits residue flours (orange, passion fruit, watermelon, lettuce, among others) were evaluated by spraying or dipping onto fresh-cut carrots.[160] Results showed that coating by dipping prevented more effectively the growth of microorganisms (mesophiles, yeast, and phychrophiles) after 15 days at 5 °C.

4.5 Antioxidant and antimicrobial coatings for meat and seafood

Meat and seafood provide high-quality proteins and valuable micronutrients essential for a healthy human diet. Red meat is an important source of iron while fish meat supplies healthy fatty acids and vitamin D. However, their chemical composition is easily prone to oxidative deterioration, especially during the post-mortem handling and storage, resulting in off-odors, rancidity, and modification of the texture, color and the characteristic brightness of a fresh product. Most of these reactions are linked to the natural oxidation of lipids and iron present in hemoglobin and myoglobin.[161] During lipid oxidation, poly-unsaturated fatty acids produce secondary products such as malondialdehyde (MDA), known to be cytotoxic and genotoxic, and small volatile ketones and aldehydes that cause rancidity and unpleasant odors. UV-light, metals, and oxygen molecules play an essential role in lipid oxidation as activators of the reactive oxygen species (ROS), which are involved in the oxidation mechanism.[162] The oxidative damage of food is determined by quantifying the amount of peroxide, ketone, and aldehyde products generated, with PV or quantifying the MDA concentration represented in thiobarbituric acid reactive substances (TBARS).[163,164] The PV scale for freshness suggests that foods with values above 8–10 mmol of O_2 per kg are classified as *spoiled.*[165]

Plant-based coatings may prevent lipid oxidation by reducing the food contact with atmospheric oxygen.[166] Furthermore, the protection against oxidation can be reinforced by incorporating natural antioxidants, such as EOs. In the work of Alotaibi and Tahergorabi, several shrimps were coated with thyme EO (2 wt%) incorporated as emulsion into a sweet potato starch-based aqueous solution by immersion during 15 minutes. The coating kept the TBARS value lower than 0.5 mg MDA per kg of shrimp after eight days of storage, while the uncoated shrimps exhibited TBARS value close to 3 mg MDA per kg of shrimp after the same storage period.[159] The potential of EOs to prevent radicals' formation was demonstrated in Mohammad Noshad *et al.*[167] Incorporating 2 wt% of citrus lemon essential oil in a Plantago major seed mucilage-based emulsion suppressed radicals' formation by 86% less meq O_2 per kg in dip-coated buffalo meat, due to the strong scavenging activity.[167]

As stated before, the high water activity, as well as the amount of lipids and proteins present in meat and seafood, make them prone to the growth of bacteria and other pathogenic microorganisms responsible for food spoilage. The main indicator of degradation and low quality of seafood is the putrefactive odor caused by spoilage microorganisms, which release small volatile organic bases, called biogenic amines.[168] The reduction of oxygen concentration in the package, by modification of its atmosphere or by vacuum, and the freezing conditions, can only inhibit part of the development of microorganisms in food.[166] In particular, psychotropic bacteria grow within a temperature range of −21 to −14 °C, while in anaerobic environments, psychotropic bacteria and anaerobic lactic acid bacteria survive, generating off-odors metabolites and severe acidification.[169] The microbial activity is usually defined as a total viable count (TVC) or total plate count, which includes the concentration of microorganisms such as bacteria, yeast, or mold spores in food in terms of colony-forming

units (CFU) per weight, volume or surface of the sample. For freshwater and marine species, the microbial limit recommended by the International Commission on Microbiological Specifications for Foods (ICMSF) is 7 log CFU per g, while humans are capable of noticing the food spoilage with TVC in the range of 6 to 8 log CFU per g of the product.[165,170] The low effectivity of sensory indicators underlines the high importance of preventing bacterial spoilage by edible antimicrobial coating. Shrimp dip-coated with sweet potato starch loaded with thyme EO has been demonstrated to inhibit completely aerobic bacteria during eight days of storage when the thyme EO concentration overcomes 4 wt%.[159]

Few articles include only vegetable and fruit by-products as a matrix of meat coatings; in their place, chitosan appears as the main component because of its widely known antimicrobial activity.[74] Licciardello *et al.* have studied the preservation effect of chitosan-based and locust bean gum-based edible coatings incorporating 7, 18, or 36 wt% pomegranate peel extract on shrimps during cold storage.[170] Results showed that chitosan coating exhibited a better inhibition response against psychotropic bacteria than locust bean gum coating. As expected, chitosan films loaded with pomegranate extract showed the best antimicrobial results against psychotropic bacteria and *Pseudomonas* spp., while LGB with pomegranate peel extract showed the same bacterial inhibition of the control chitosan coating.[170]

5 Summary and perspectives

Non-edible agro-food wastes, such as industrial discards from processing fruits, vegetables or grains, represent a promising source of raw materials that is currently underutilized. These resources, which include structural biopolymers (such as polysaccharides, lignin and proteins), and a wide variety of bioactive molecules (such as the antioxidant carotenoids and anthocyanins and antibacterial essential oils), are the subject of research that aims to incorporate them back into new added-value products according to a circular economy model. The review covers upcycling of such biomass from agricultural plant residues to films or coatings, intended for food packaging to improve food safety, extending shelf life and reducing spoilage. Active food packaging was also addressed, when plant biomolecules with peculiar antimicrobial and antioxidant activities were incorporated into the developed films or coatings.

Approximately 2 billion tons of only lignocellulosic agricultural waste, such as corncob, rice husk, rice straw, sugarcane bagasse, wheat straw, *etc*., are produced annually worldwide.[173] Although estimations of the total industrial fruit and vegetable non-edible discards are missing in the literature, such agrowaste biomass quantities are much higher compared to the 147 million tons of plastic produced annually for packaging.[5] Therefore, they could be the ideal raw materials to be upcycled into plastic alternatives. This approach would also prevent competition between the food industry and the material industry. For this reason, this review focused on the scientific publications that used non edible agricultural biomass that is currently discarded or underutilized, to develop methods to convert such biomass into materials, without the use or generation of harmful substances, in accordance to the principles of green chemistry. Few literature examples that have used potentially unsafe substances or fossil-derived non-biodegradable polymers have been included, to highlight the effort towards a greener chemistry. When that was the case, it was always highlighted.

The processing with green chemicals or low energy methods of different agrowaste biomasses for their partial or preferably complete conversion into bioplastic materials or active coatings for food preservation, is an area of research with enormous potential and opportunities, but also great challenges.

The first challenges arise from the high variability of raw materials' composition, which require processing strategies to be mitigated. As shown in the review, the composition of the starting biomass largely determines the properties of the developed materials, and therefore, standardized methods need to be developed to obtain bioplastics with specific properties from a wide range of diverse plant resources. In the article, a distinction was made between biomass that was fully converted into films or coatings, and biomass components that were used as fillers in biocomposites. The former strategy has the ambition of producing packaging materials made entirely of plant biomass, whereas the latter uses a lower percentage of plant waste (typically not higher than 50 wt%). Despite the attractiveness of using materials made entirely of plant constituents, another challenge to address in this case is the moisture sensitivity and poor mechanical properties that such biocomposites occasionally demonstrate. Indeed, we have discussed the main physicochemical properties of the developed materials, as well as the reported methods to improve their mechanical properties and humidity resistance. In the case of the use of biomass components as fillers for the development of packaging films, some of them were developed with the traditional methods of processing of thermoplastic polymers, as melting processing, that were adapted to plant-originated biocomposites. Such materials usually have better mechanical properties and are less moisture sensitive than the ones made using entirely plant biomass and solvent processing methods, but can face the challenge of most difficult biodegradation.

The development of such materials needs to be supported by life cycle assessments (LCA), to quantify how the new materials can improve sustainability at a system scale, to determine the most sustainable transformation or conversion processes and identify possible process shortcomings. Unfortunately, LCA of the proposed packaging is almost never considered in the research articles. LCA is important since it highlights the best circular pathways that convert by-products derived from biomass processing back into the Market that generated them or into other external ones. Unfortunately, the literature reviewed here did not show a significant focus on

examining and quantifying environmental impact parameters for the different circular scenarios. However, it is noted that greater efforts are still needed to broaden and deepen the vision of real opportunities and viable challenges. Most of the processes reviewed are still on a laboratory scale, requiring major efforts to convert them to an industrial scale.

In addition, it is still necessary to delve into issues related to the biodegradability of such materials. Materials prepared from plant residues have the advantage to be prone to rapid biodegradation,[104] but at the same time it has to be assured that when they are used for food packaging they maintain the structure and functionality at least during the food shelf life and ideally even for longer, so that recycle or reuse can be an option. Upon disposal, the biodegradation process should be clearly distinguished between industrial and home compost, the first requiring dedicated facilities and the second household compost conditions. In this way, the consumer will have all the necessary information for an easy and correct disposal. Pushbacks that are seen with the disposal and separation of some commercially available bioplastics, like PLA,[174,175] should be overcome by new focused investments but also support actions from government organizations and decision making centers. It is expected that once some numerous promising materials and packaging alternatives will be developed, new plants to handle their biodegradability will be developed, as is currently happening with polymers such as PLA and PHAs.

A strong connection between academia and policymaking is sorely needed. Currently, the scientific community continues to focus its efforts on developing solutions and improvements for new bioplastics based on agrowaste biomass. However, this initiative must be accompanied by governmental actions that promote the valorization this waste, or rather "new raw materials", on a large scale. In addition, it is still necessary to focus on the economic analysis and the social impact of the production, use, and disposal of these materials. Undoubtedly, the joint and integrated work between these sectors will lead to the changes that our society demands for the coming decades.

Abbreviations

AAE	Ascorbic acid equivalent
ABTS	2,2′-Azino-bis(3-ethylbenzothiazoline-6-sulfonic acid radical
a_w	Water activity
CNC	Cellulose nanocrystals
CNFs	Cellulose nanofibers
CNPs	Cellulose nanoparticles
DPPH	2,2-Diphenyl-1-picrylhydrazyl radical
Eb	Elongation at break
EOs	Essential oils
FAO	Food and agriculture organization of the United Nations
FRAP	Ferric reducing antioxidant power
GAE	Gallic acid equivalent
GRAS	Generally recognized as safe
HDPE	High-density polyethylene
HG	Homogalacturonan
ICMSF	International commission on microbiological specifications for foods
MCC	Microcrystalline cellulose
MDA	Malondialdehyde
MPF	Mango peel flour
MPFS	Mango peel flour with the antioxidant extract of mango seed
O_2P	Oxygen permeability
PE	Polyethylene
PEAs	Polyesteramides
PET	Polyethylene terephthalate
PHAs	Polyhydroxyalkanoates
PLA	Polylactic acid
PP	Polypropylene
PPO	Polyphenol oxidase
PV	Peroxide value
PVC	Polyvinyl chloride
RBW	Rice bran wax coating
RG I	Rhamnogalacturonan I
RG II	Rhamnogalacturonan II
ROS	Reactive oxygen species
TBARS	Thiobarbituric acid reactive substances
TFA	Trifluoroacetic acid
TPC	Total polyphenol content
TS	Tensile strength
TVC	Total viable count
WG	Wheat gluten
WVP	Water vapor permeability
YM	Young's modulus

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Conflicts of interest

The authors declare no conflict of interest.

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