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Sustainable biodegradable coatings for food packaging: challenges and opportunities

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This review article provides a thorough overview of barrier coating materials that have been used in food packaging with a focus on biodegradable (bio-based or petroleum-based) materials, such as lipids, proteins, polysaccharides, agriculture waste and polyesters. The goal is to provide an opportunity to acknowledge progress made in this field, focusing on modifications made to coatings. These modifications aim to address the shortcomings of biodegradable substrates (either plastic or paper) and improve their performance, enabling them to compete with traditional petroleum-based food packaging materials. This includes their barrier against water vapor and oxygen, mechanical and surface characteristics (sealability and adhesion), as well as antimicrobial properties. The barrier of most biodegradable polymers underperforms in comparison with petroleum-based non-biodegradable polymers, which possess either high water vapor barrier or high oxygen barrier. Coating technology is a promising solution particularly in barrier improvement of biodegradable polymers. Currently, there are only metallized, or inorganic nanosheet coatings available for biodegradable films that meet food packaging requirements. There are some challenges in this field, for example, being able to retain the coating's biodegradability despite applied modifications to improve it's performance, the large-scale fabrication of biodegradable coatings, the coating's delamination and heat-sealability during service time, and the migration of the coating into the packaged food. Moreover, green chemistry and its sustainability needs in biodegradable polymeric coatings are also discussed regarding new ideas and possible directions for widespread application of coatings in food packaging. This is the first review that specifically summarizes biodegradable coatings on plastic and paper substrates with a focus on coating modifications to improve the performance of the base substrate to meet the required properties for food packaging applications.

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1. Introduction

1.1 From food waste to food packaging

"We have woken up to plastic waste. Is food waste next?" (Liz Goodwin).[1] It is time to take the pledge to choose the health of our planet over plastic. Nowadays, it is evident to all that plastic waste has dreadful consequences for our planet. Additionally, we are facing another equally urgent waste issue, which is food. According to the world counts website, one-third of the world's food is not only never consumed, but is wasted in each step of the food life cycle.[2] This includes (I) agricultural production such as crops, that can be damaged in farms by pests, diseases and factors linked to the weather, soil, climate, water availability, and natural disasters resulting in 1.2 billion tonnes of food waste per year ~15%,[3] (II) processing and manufacturing (food waste of ~5%),[3] (III) storage and distribution that is food waste from retail to consumer stages of the supply chain (~17%),[3] (IV) preparation and cooking and (V) end-of-life.[2] Food packaging is used worldwide to protect food against environmental contamination from outside sources such as odors, gases, aromas, humidity, light, physical damage, and microorganisms.[4–6] Also, food packaging is the main contributor to ensuring the safety and quality of food, as well as prolonging its shelf life, thereby lessening food wastage and losses.[6,7]

Overall, plastic polymers, which are not biodegradable, have the largest amount of usage in the food packaging industry.[8,9] Petroleum-based plastics (*e.g.*, polyvinyl chloride (PVC), polypropylene (PP), polyvinylidene chloride (PVdC), polyethylene (PE), high- and low-density polyethylene (HDPE and LDPE), polystyrene (PS) and polyethylene terephthalate (PET)) are still commonly used in food packaging, while most never see a second life and are associated with environmental concerns.[10] To be more precise, the biodegradation rate of petroleum-based plastics ranges from tens to thousands of years.[11] In addition, these plastics can enter the ocean and biodegrade into microplastics, which end up in the stomach of marine organisms and eventually enter the human food chain.[11] This is what triggers the urgent need for bio-

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degradable materials. The planet and its inhabitants would benefit significantly from the prompt discovery of environmentally friendly and sustainable alternatives to traditional plastic food packaging materials.

1.2 Development of biodegradable food packaging – limitations and strategies

As reported by the IUPAC, "a bioplastic is a biobased polymer derived from the biomass or issued from monomers derived from the biomass and which, at some stage in its processing into finished products, can be shaped by flow". Notably, using the term bioplastic is discouraged, since it represents that any polymer produced from biomass is ecofriendly. Hence, the IUPAC proposes the term "biobased polymers".[12] Utilization of biobased polymers as food packaging materials has seen various functional limitations over the past years, such as brittleness, difficult heat sealability, thermal instability, low melt strength, and poor barrier characteristics (*i.e.*, high permeability to water vapor and oxygen)[13–16] (Fig. 1). These shortcomings restrain them from being a viable substitute for petroleum-based plastics in food packaging applications.[17,18] To enrich the functional properties of biobased polymers, particularly barrier capacities against gasses and water, several strategies have been proposed in the available literature, for instance, development of biobased films and coatings,[7,17] incorporation of nanoparticles (*e.g.*, reinforcement of biopolymers with nanoclay[17,19]), chemical modification[20] (*e.g.*, grafting fatty acid to improve the water vapor barriers[21]), physical modification (*e.g.*, heat treatment and irradiation[22]), and blending two or more biobased materials[23] (Fig. 1). Among the aforementioned strategies, coatings could add several advantages to the substrate such as resistance against permeation of gases (*i.e.*, O_2, CO_2), water vapor, aromas, volatile organic compounds (VOCs), oils, and light (*i.e.*, UV radiation). Furthermore, coatings can enhance the mechanical (*e.g.*, friction resistance, tensile strength, and scratch resistance), optical (gloss and haze), surface (adhesion and sealability) and thermal (*e.g.*, flame barrier) properties of the base substrate. Finally, coatings can provide new functions for the packaging such as antibacterial or antimicrobial properties.[7] An "antibacterial" material is defined as a substance that interferes with bacterial growth and survival by selectively destroying bacteria.[24] In contrast, "antimicrobial" is a broader term, encompassing materials that inhibit the growth of various microorganisms, including bacteria, fungi, and algae.[25] Biobased coatings could be made from different biopolymers, namely polyesters, polysaccharides, lipids and proteins (Fig. 1).

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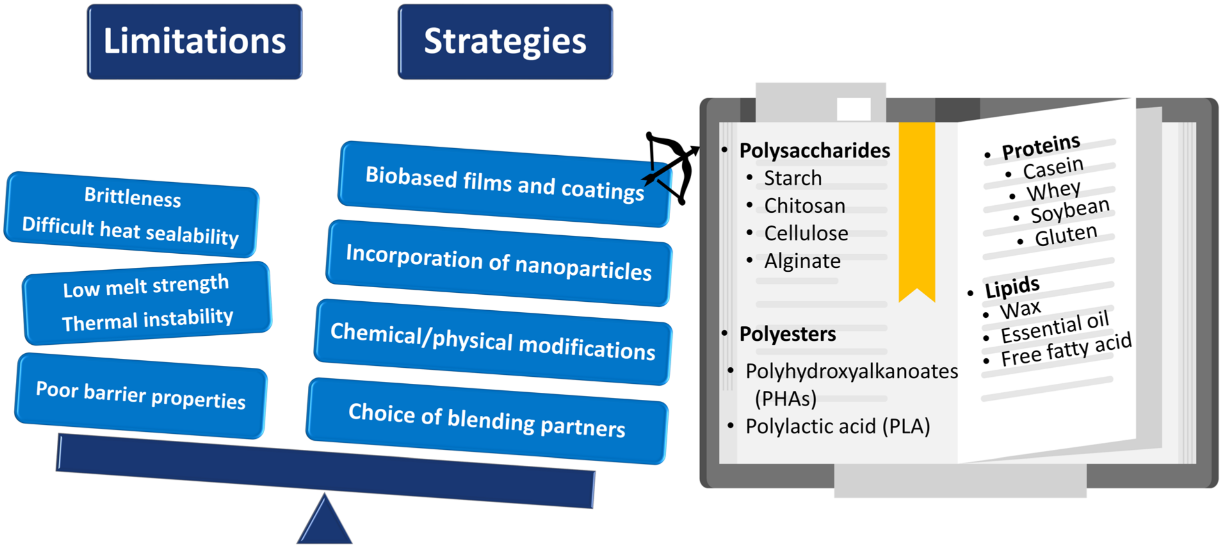

Fig. 1 Biobased polymers' limitations and strategies for food packaging applications.

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1.3 Development of green coating alternatives to petroleum-based coating

Synthetic polymeric barrier coating materials, such as polyfluoroalkyl (PFA) substances-coated paper wraps and epoxy-based resin (bisphenol-A (BPA))[26]-coated canned goods cannot be recycled or repulped and can have harmful effects on human health.[27,28] Polyvinyl alcohol (PVA) is a more environmentally friendly option that is widely used as petroleum-based biodegradable coatings for flexible/rigid paper packaging to protect food against oxygen permeation.[29] Bio-based non-biodegradable polymers such as bio-polyethylene (Bio-PE) and bio-polyethylene terephthalate (Bio-PET) have rarely been used as coatings for food packaging applications, and have not been commercialized. An example of this application is the development of oxygen scavenger multilayer films using Bio-PE as the food contact layer incorporating gallic acid as the oxygen scavenger.[30] The greatest number of bio-based biodegradable barrier coatings come from proteins, polysaccharides, lipids, and their composites.[7] Protein coatings such as the zein-based coating from FloZein Products[31] have been applied on cardboard containers for greasy food, on fresh/dried fruits and vegetables to provide a long-lasting moisture and microbial barrier as well as on fresh fish/meat to reduce oil absorption during frying. Gum ghatti is a complex polysaccharide used in the paper industry as a moisture barrier coating.[32] Paper and paperboard coated with Solenis TopScreen biowax barrier coatings are available in the market. They are repulpable, recyclable, and industrially compostable with EN 13432 certification.[33] However, to the best of our knowledge, there are no other wax coating materials tested as biodegradable. More research is needed to perform biodegradability tests on natural wax coating materials to ensure their biodegradability strictly under ASTM, ISO, European standard methods. Polyesters are also used as coatings for food packaging applications. For

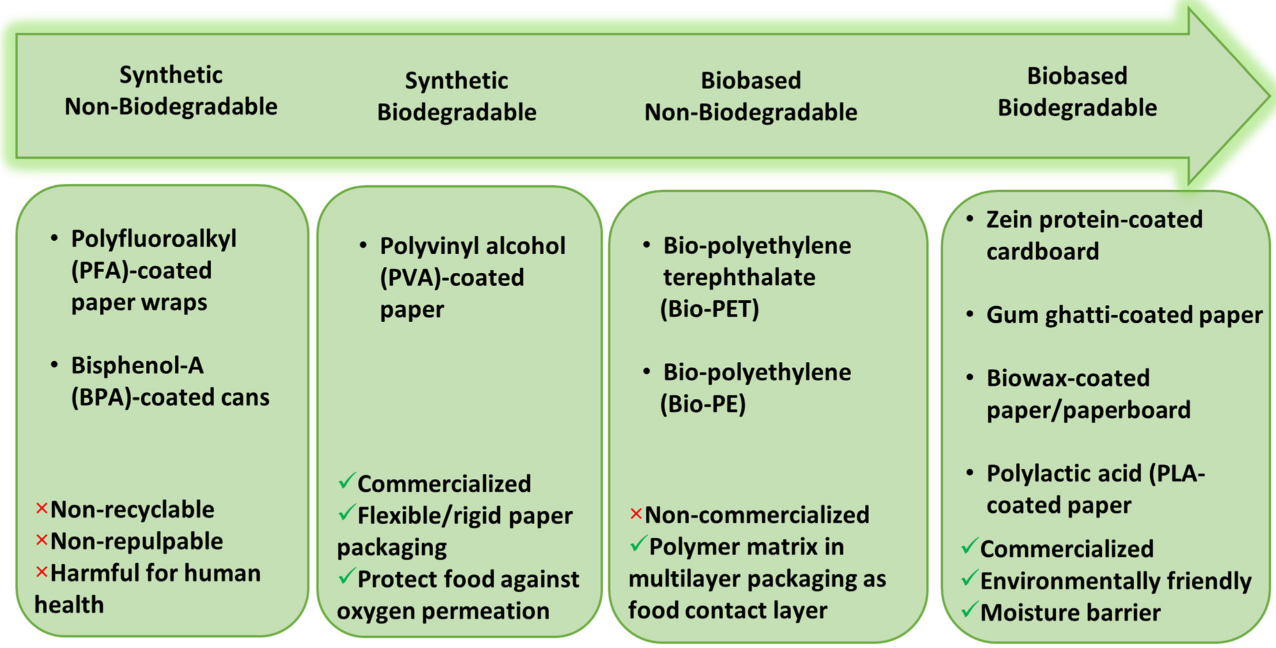

Fig. 2 Transition from synthetic non-biodegradable coatings to biobased biodegradable coatings for food packaging applications.

example, poly(lactic acid)-coated paper has been commercialized as stand-up bags for dried fruits, pulp molded trays and paper glasses for cold liquids.[34] Polyhydroxyalkanoates and starch-based aqueous coatings have shown odor/taste protection, oil/grease resistance, and gluability/heat sealability. Nevertheless, aqueous coatings cannot provide high water/water vapor barrier properties.[34] Overall, in both academic and industrial sectors, a significant transition is evident, moving away from synthetic non-biodegradable coatings towards biobased, biodegradable alternatives (Fig. 2). Ongoing endeavors are focused on improving the performance of environmentally friendly coatings for applications in food packaging.

In summary, the development of biodegradable packaging materials has attracted interest worldwide, as it is known to lessen the environmental impact associated with traditional petroleum-based plastic packaging. Nevertheless, getting sufficient properties from biobased biodegradable polymers that are required for food packaging applications is challenging. Various technologies are being developed to compensate for the biobased biodegradable deficiencies and enrich their functional properties to be able to compete with traditional plastic packaging. Coatings serve as an emerging technology to improve the functional properties of the biodegradable substrate, particularly regarding barrier properties against oxygen and water vapor, thereby improving food shelf life. The manufacture of paper, paperboard, cellulose thin films, plastic coatings, fibrous fabric sheets, metallic foils, *etc*. are some of the main applications for coating technology. Using this technology, two or more layers with specific and complementary properties can be combined (*i.e.*, multilayer) to obtain a single-layer structure, resulting in enhancing the performance of the substrate. Various materials are used as a coating such as bio-based biodegradable biopolymers (*i.e.*, lipids, proteins, polysaccharides, biomass, and agriculture waste), bacterial polymers (*i.e.*, polyhydroxyalkanoates), and synthetic biodegradable polymers (polybutylene adipate-*co*-terephthalate (PBAT), polycaprolactone (PCL), polybutylene succinate (PBS)), which are reviewed in this paper. Through reviewing the previous strategies used to develop biodegradable coating materials, the pros/cons and efficiency of different coating methods and the challenges of their commercialization are summarized to guide the future design of coatings' modifications, widening their commercialized applications.

2. Principle and stratagem to developing green coatings

One of the main strategies for improving the barrier properties of biodegradable food packaging is surface coating. In principle, applying an additional thin layer on one or both sides of bio-based films or other packaging materials (*i.e.*, paper, paperboard) is defined as a coating process.[17] There are various coating techniques including chemical/physical vacuum deposition, solution coating (*e.g.*, layer-by-layer assembly, slot-die coating, brush/bar coating, spray coating, spin coating and dipping), electrohydrodynamic processing (*e.g.*, electrospraying, electrospinning) and other techniques such as melt extrusion coating and hot pressing (Fig. 3). Coating techniques are more versatile than lamination or coextrusion in terms of manipulating or developing multilayer structures with different thicknesses from nano to millimeters.[35]

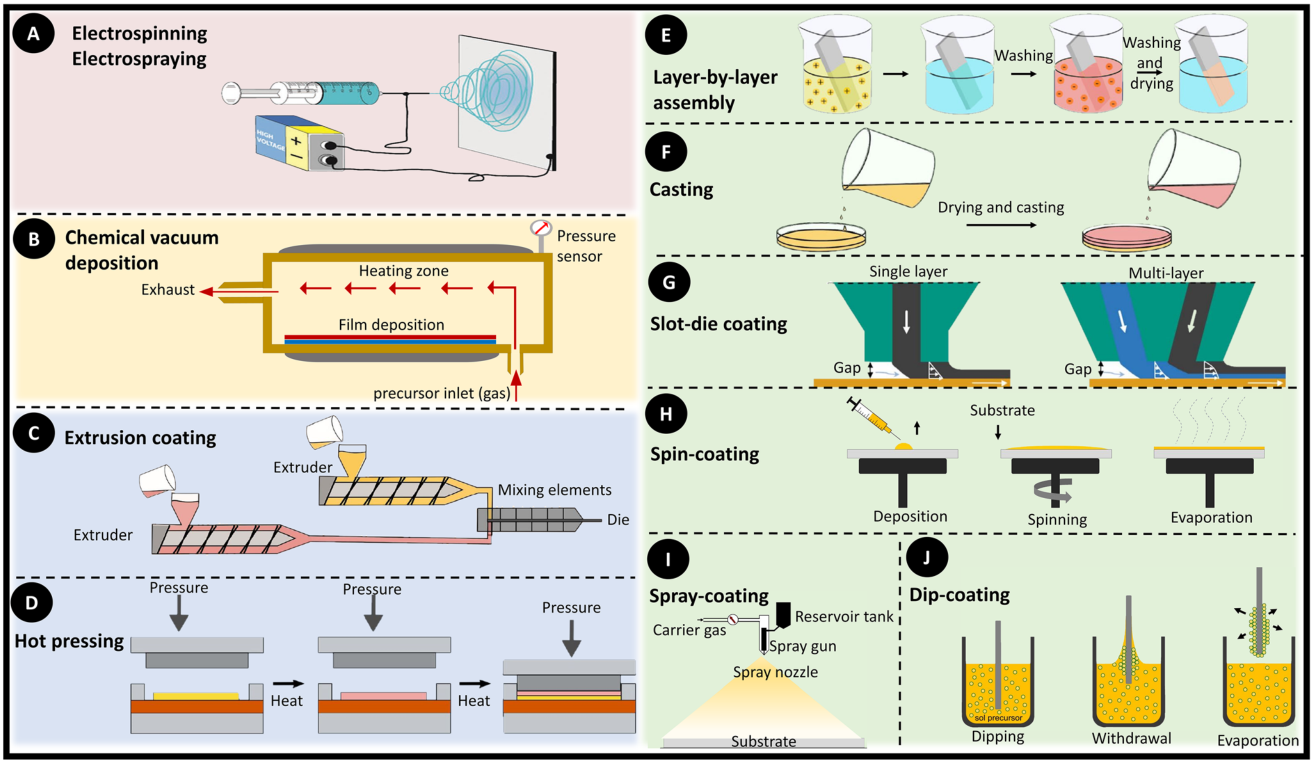

Fig. 3 Different coating techniques for the preparation of single-layer or multilayer coatings. Schematic figures are adapted from the following references. (A) Electrohydrodynamic processing including electrospinning, electrospraying; reproduced from ref. 46 with kind permission from John Wiley and Sons, copyright 2020, open access. (B) Chemical vacuum deposition (CVD) is redrawn by the authors from ref. 47 with kind permission from RSC, copyright 2016. Other techniques include (C) extrusion coating and (D) hot pressing[48] and solution coatings including (E) layer-by-layer assembly, (F) casting; (figure C–F are reproduced from ref. 48 with kind permission from Taylor & Francis, copyright 2021). (G) Slot-die coating, reproduced from ref. 49 with kind permission from John Wiley and Sons, copyright 2020, open access. (H) Spin-coating, (I) spray-coating and (J) dip-coating (figure H–J are reproduced from ref. 50 with kind permission from Springer Nature, copyright 2021, (license number 5581701004745)).

Coating materials include inorganic nanoparticles, small organic molecules, and different macromolecules. Different coating materials and coating techniques along with their advantages/disadvantages have been reviewed and summarized in previous literature.[34–38] Here we have reviewed the coatings derived from specifically biodegradable polymers for paper/plastic substrate and their corresponding modifications to improve the performance of the substrate.

In the biodegradable polymer field, coating technology can be divided into two categories: (1) coating a high barrier layer onto the biodegradable polymer film/sheet, and (2) coating the high barrier biodegradable polymer (*e.g.*, polyhydroxybutyrate-*co*-hydroxyvalerate (PHBV), bionanocomposites or waxes) on the paper/paper board. The interfacial interactions between the substrate and the coating material can significantly affect the barrier of the whole structure, because the separation of coating and the matrix results in poor oxygen/water vapor barrier of the whole structure. Interactions of molecular assembly deriving forces such as electrostatic[39] and hydrogen bonding,[40,41] corona treatment,[42] and silane hydrolysis[43] have been studied so far to improve the interface adhesion between the coating material and the substrate.

It is noteworthy that, although coatings and films are sometimes used as equally the same, their method of application is thoroughly different. A material that is obtained as a standalone solid laminate followed by applying it to foodstuff (or a substrate *e.g.*, paper/paperboard and biobased polymers) is known as a film. However, a coating is applied to food stuff (or paper/paper board and biobased polymers) *via* a method that may or may not contain a liquid and is not a stand-alone structure.[44,45] In the literature, this differentiation in definition has only been highlighted for edible films and coatings on food as the substrate. In the above description, we generalized it to other substrates as well.

3. Different types of biodegradable coatings and their modifications

3.1 Coatings from nature

3.1.1 Lipid-based coatings. A summary of all biopolymers from nature that can be used as coating materials is shown in Fig. 4, which will be discussed throughout section 3.1.

Lipid-based materials have great potential in biopackaging applications, due to their hydrophobic nature, which results in impressive barrier properties against moisture transfer.[7,52] Lipid compounds are extracted directly from biomass originating from animals, insects, and plants, which are considered natural sources.[44]

Lipids contain diverse functional groups such as mono-, di- and triglycerides, fatty acids, fatty alcohols, phospholipids, terpenes and cerebrosides.[44,52] Fig. 4 shows the most common lipids that have been used in coating formulations for food packaging applications. Lipids, which are composed of fatty acids, originate from vegetable oils, essential oils, and natural waxes (*e.g.*, candelilla or carnauba wax, and beeswax).[44] Soybean oil,[53] corn oil,[54] and sunflower oil[55] are some of the most common vegetable oils that are used as coatings for food packaging applications. Among other lipid compounds, the high hydrophobicity of waxes makes them the most efficient barriers against water vapor permeation.[7,52,56]

Pure lipid coatings are not commonly used as they are mechanically weaker and have low structural integrity in contrast with proteins and polysaccharides.[52] In this regard, composite coatings derived from hydrocolloids (proteins or polysaccharides) and lipids are more advantageous than the addition of lipids into proteins and polysaccharides, as the latter may cause low strength.[52] Lipids play the role of a barrier against moisture transfer and hydrocolloids play the role of a supporting matrix and provide a barrier against gases in the composite structure. Lipids and hydrocolloids are processed by making either bilayers or emulsions[52,57] (Fig. 5).

Functional properties, including barrier properties, of coatings derived from lipid compounds are influenced by their chain length, saturation degree, physical state, structure (*e.g.*, degree of polarity), crystal dimensions, lipid distribution into the coating (*e.g.*, homogeneity or heterogeneity), as well as humidity and temperature.[52] The high resistance of wax coatings is due to either their hydrophobic nature (absence or low number of polar groups) or their molecular organization (waxes possess a tight orthorhombic crystalline arrangement, in which their direction is perpendicular to the gas flow and therefore do not allow the gas transfer)[58] (Fig. 5).

Beeswax coating on whey protein isolate-cellulose (WPI-cellulose)-based film decreased the water vapor transmission rate (WVTR) by 92–95%, and was then coated on commercial cereal box paper board.[60] Although WPI has a good film-forming property, its high WVTR in the presence of plasticizers limits its applications. Incorporating a lipid component is a smart modification for achieving a high barrier against moisture. A biodegradable starch-based glue was used as an interfacial adherent between beeswax and the WPI layer.[60] Biodegradable trays of thermoplastic starch/polylactic acid (TPS/PLA) coated with 1% beeswax in ethyl alcohol and Tween80 emulsion showed the lowest solubilisation capacity in water, which contributed to water vapor permeation (WVP) being reduced by 97.46%.[61] The concentration of beeswax emulsion showed a significant effect on the water vapor barrier properties of the trays, in which using 2–3% beeswax emulsion caused an inferior adherence to the substrate and delamination.[61] PLA

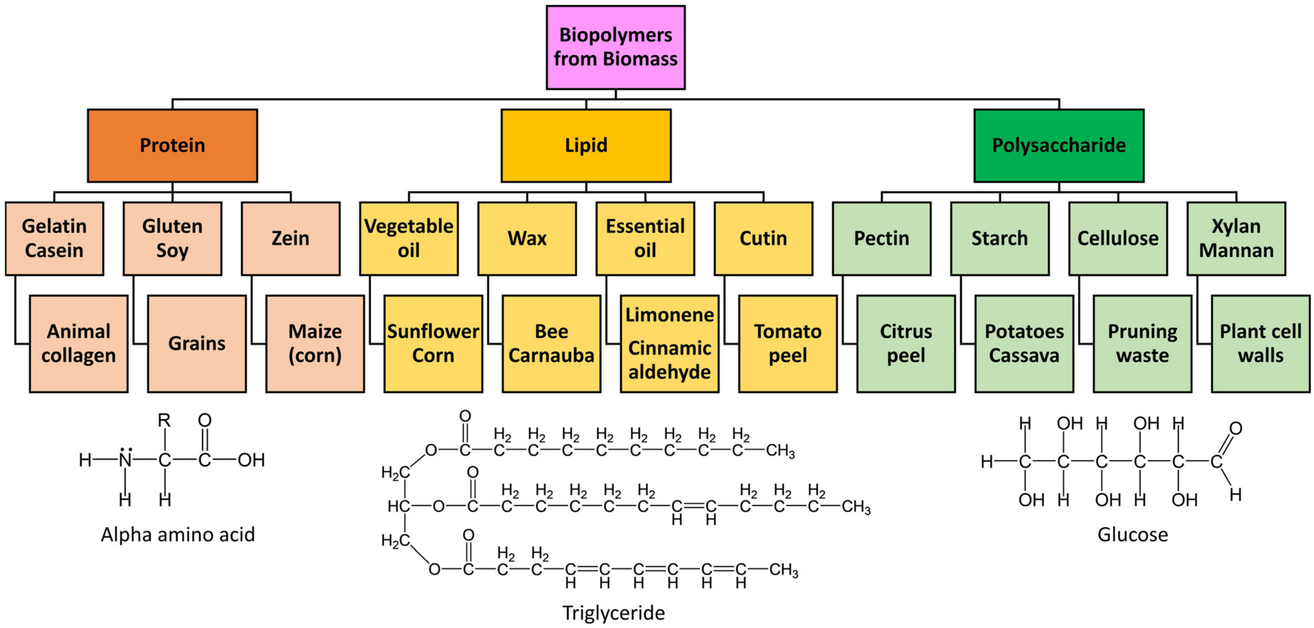

Fig. 4 A categorization of biopolymers obtained from biomass. Biopolymers are categorized in three main groups, namely proteins, lipids and polysaccharides. Some examples are shown under each categorization followed by their origin underneath. The typical chemical structure of each group is drawn in ChemDraw by the authors. Proteins are made of a major building block called alpha amino acid. Triglycerides are the most common type of lipids. Finally, polysaccharides are long chains of monosaccharides, of which the most common is glucose. Figure is redrawn from ref. 51, with some added components by the authors with kind permission from MDPI, copyright 2020, (open access).

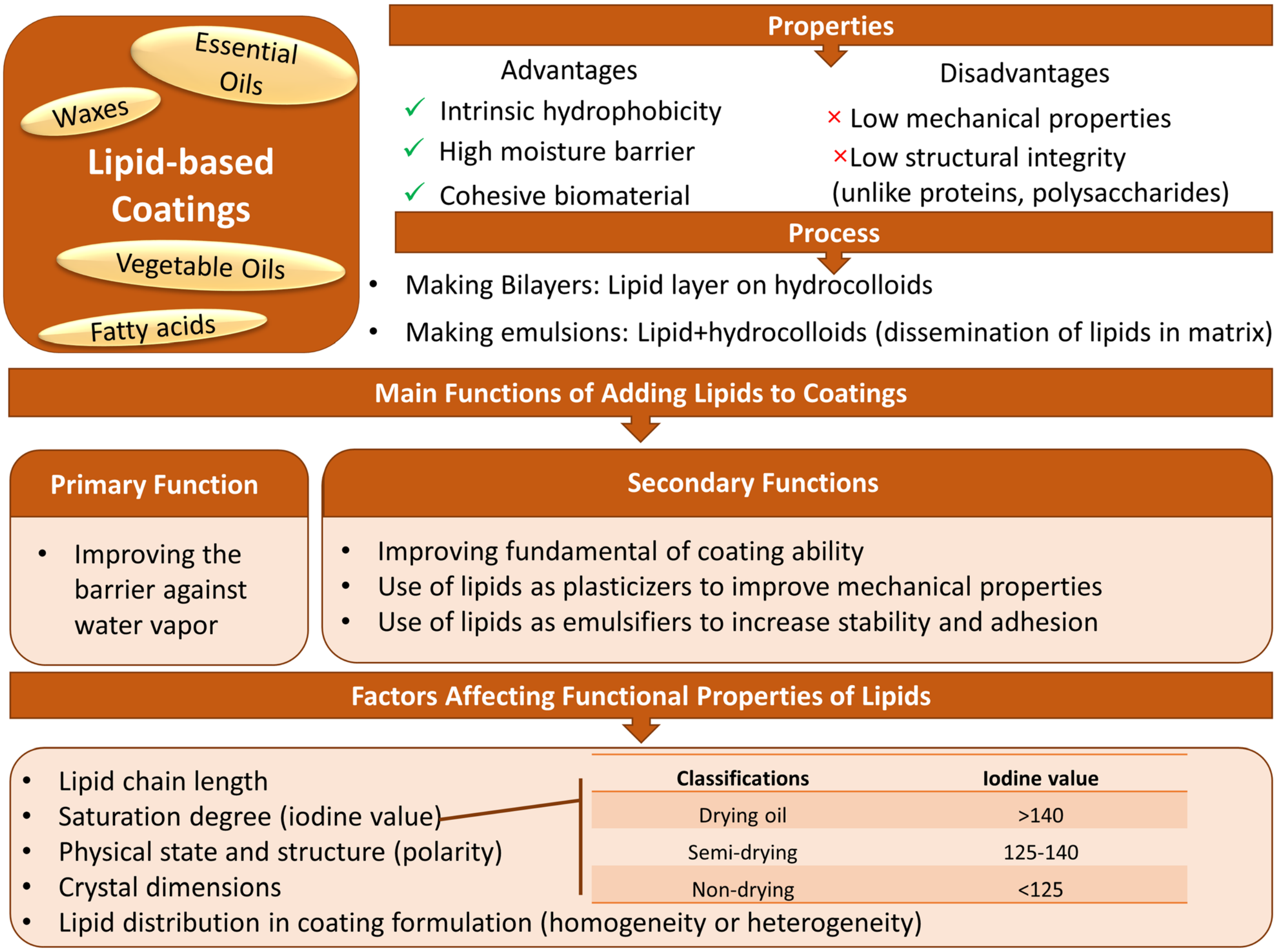

Fig. 5 Characteristics of lipid-based coatings including their natural properties, processes of making coatings from lipids, their main functions and factors affecting their functions. Data of iodin values for different types of oils are from ref. 59.

films coated with a crosslinked chitosan/beeswax layer had an increased water vapor/oxygen barrier as well as abrasion resistance through a reduction of swelling in PLA films. This resulted from the crosslinked chitosan, which showed more profound effects on oxygen transmission rate (OTR) reduction. A layer of beeswax coating reduced the WVTR further. However, there was not a significant difference in OTR between samples with or without beeswax coating.[62] Hydroxypropyl methylcellulose incorporating beeswax coatings showed improved moisture barrier from 20 to 50% compared to the formulation without beeswax. By increasing beeswax content from 20 to 60%, the moisture barrier improved significantly, while the oxygen barrier and mechanical properties reduced.[63] When considering materials with high hydrophobicity, particularly for use as robust barriers against water vapor, waxes are the primary substances that come to mind.[64] Nevertheless, there are still some issues that need to be considered to create fully biobased and biodegradable coatings based on natural waxes (Box 1). The strategies that have been addressed in the literature are also summarized in Box 1.

Box 1 Biobased and biodegradable coating based on waxes: Limitations and strategies

Limitations:

- In solution coating methods, waxes are dissolved in a solvent, which is either chlorinated or non-chlorinated hydrocarbons.[64] To produce a sustainable biobased and biodegradable coating, "green" solvents such as water, supercritical fluids, ionic liquids, liquid polymers and biomass-derived solvents[65] should be used.
- Most waxes have a low melting point (*e.g.*, beeswax 45.5–70 °C,[66] candelilla 54.5–76 °C (ref. 66)) and can leach away easily, which is a disadvantage for thermal stability of coatings.
- By increasing the wax content of the coating composition, one can reduce water vapor permeation (WVP) for the packaging material; however, poor adhesion of waxes to the substrate limits their viable concentration in coating formulations.
- A slight change in temperature can cause waxes to become soft or brittle and suffer from low abrasion resistance once coated on the substrate.[64]

- The biodegradability of waxes needs to be studied specifically according to standard methods, to ensure the biodegradability of the whole packaging material after being coated by natural waxes. A small number of studies have reported the effect of wax coating on biodegradability of the packaging material[67] based on standard methods. The biodegradability should be ≥90% (by respirometer) after maximum 180 days for a material to be considered biodegradable (ASTMD6400).

Strategies:

- Low melting point of waxes can also be considered as a positive aspect, as they can be easily emulsified with water instead of using hydrocarbon solvents.[64]
- To tackle the leaching problem of waxes, they can be mixed with other hydrophobic polymers such as polydimethylsiloxane[68] for encapsulation and improve wax stabilization. In this regard, the wax's desire to migrate to the surface results in improved coating hydrophobicity.[64]
- Dispersion of wax in alcohol is another positive point, as it allows other polar compounds to be processed in alcohol along with waxes.[64]
- By altering the crystallization of wax, it can act as a coating with rough surface similar to the lotus leaf.[64]

Oils derived from a wide range of annual plant seeds have been used in the coating industry for centuries.[71] The high importance of seed oils lies in their low cost, high availability, renewability, and their high annual production across the world. Seed oils contain triglyceride molecules (Fig. 6) mixed with different fatty acid residues. The most common seed oils are derived from soybean, tung, corn, linseed, and castor.[72] Fig. 6 shows the typical seed oil's chemical composition containing esterified glycerol with 3 molecules of fatty acids as well as the normal fatty acid composition of several of the most often used seed oils, along with their chemical designations, which are either saturated or unsaturated. In addition, fatty acid chains can contain various functional groups, such as epoxy or hydroxyl. Fatty acid distribution determines the chemical/physical properties of seed oils. To explain further, the position and number of $C{=}C$ double bonds within the aliphatic chain has a noticeable effect on the final properties of the oil.[73] The amount of iodine reacted by the double bonds in 100 g of oil corresponds to the average degree of unsaturation determined by the iodine value. There are three classifications for oils depending on their iodine value,[59] shown in Fig. 5.

In industry, it is preferred to produce coatings with low solvent content. For instance, reducing the viscosity of the polymer is effective in decreasing the organic solvent content in the coatings. Polymers with a narrowed molecular weight distribution or those with a low molecular weight can be used to produce a low-viscosity coating composition.[71] Moisture-resistant paper was prepared by coating silylated soybean oil (53.1% reduction in WVTR), which did not show any changes in the oil's viscosity and therefore the coating process was performed in one step with no additional diluent, solvent, or oil emulsifier. The film formation mechanism for polymeric solutions through evaporation of the solvent/water results in volume shrinkage and film deformation or unwanted coating cracks on the surface.[74] To increase the shelf life of guavas, coatings based on cassava starch incorporating beeswax as a hydrophilizing agent and sunflower oil as an emulsion former for coating formulations were developed. The coatings showed improved barrier against moisture and increased the guavas' shelf life.[75]

Another category of lipid materials are essential oil compounds derived from plants; these are known as naturally occurring oils that have antimicrobial benefits.[76] For example, cinnamaldehyde, a main ingredient of cinnamon bark oil, showed antibacterial, antifungal, antiparasitic, insecticidal, antiviral, anti-diabetic, anticancer, and pro-wound healing properties.[77] A summary of lipid-based coatings used to improve barrier properties is listed in Table 1.

3.1.2 Protein-based coatings.

In this section, we have summarized a list of breakthroughs in protein-based coatings for food packaging applications. Protein-based coatings are divided into two categories: proteins from plants and animals; wheat gluten (WG), corn, soy proteins and zein as plant proteins, and casein, whey, keratin, and gelatin as animal proteins (Fig. 4). Biopolymers based on proteins are the most effective due to their high gas barrier properties comparing with polysaccharides and lipids. Soy-protein-based films showed 260-, 540-, 500- and 670-times reduced oxygen permeability in comparison with low-density methyl cellulose, starch, polyethylene and pectin, respectively. In addition, films based on proteins possess better mechanical properties than those based on lipids or polysaccharides.[79] The challenge of protein-based coatings is their brittleness and intrinsic hydrophilicity, which causes poor barrier properties against water vapor.

The strategies addressed for the above challenges of protein-based coatings are categorized as follows in the previous literature:[80] (I) chemical modification of proteins using chemical agents (*e.g.*, glutaraldehyde, $CaCl_2$) or inserting functional groups into protein side chains to form covalent and non-covalent crosslinking to improve their mechanical properties; (II) addition of another polymer (*e.g.*, chitosan, cellulose, alginate) or a plasticizer (*e.g.*, sorbitol, glycerol) to improve their mechanical barrier properties and reduce costs; (III) addition of natural antioxidant (*e.g.*, vitamin E) and antimicrobial agents (*e.g.*, nisin) to proteins to improve the shelf life of packaged food; and (IV) modification of the protein's surface with lipid molecules, polysaccharides or proteins to improve barrier properties and interface adhesion. Protein-based coating/film processing is based on two standard approaches: firstly, the "wet or solvent process", in which proteins are dispersed or solubilized in a solvent, and secondly, the "dry process", which is based on forming a thermoplastic followed by casting[81] (Fig. 7).

The coating of plasticized whey protein over a commercial compostable plastic film based on PLA improved the resistance of PLA against oxygen permeation by 84.37%. Any modifications

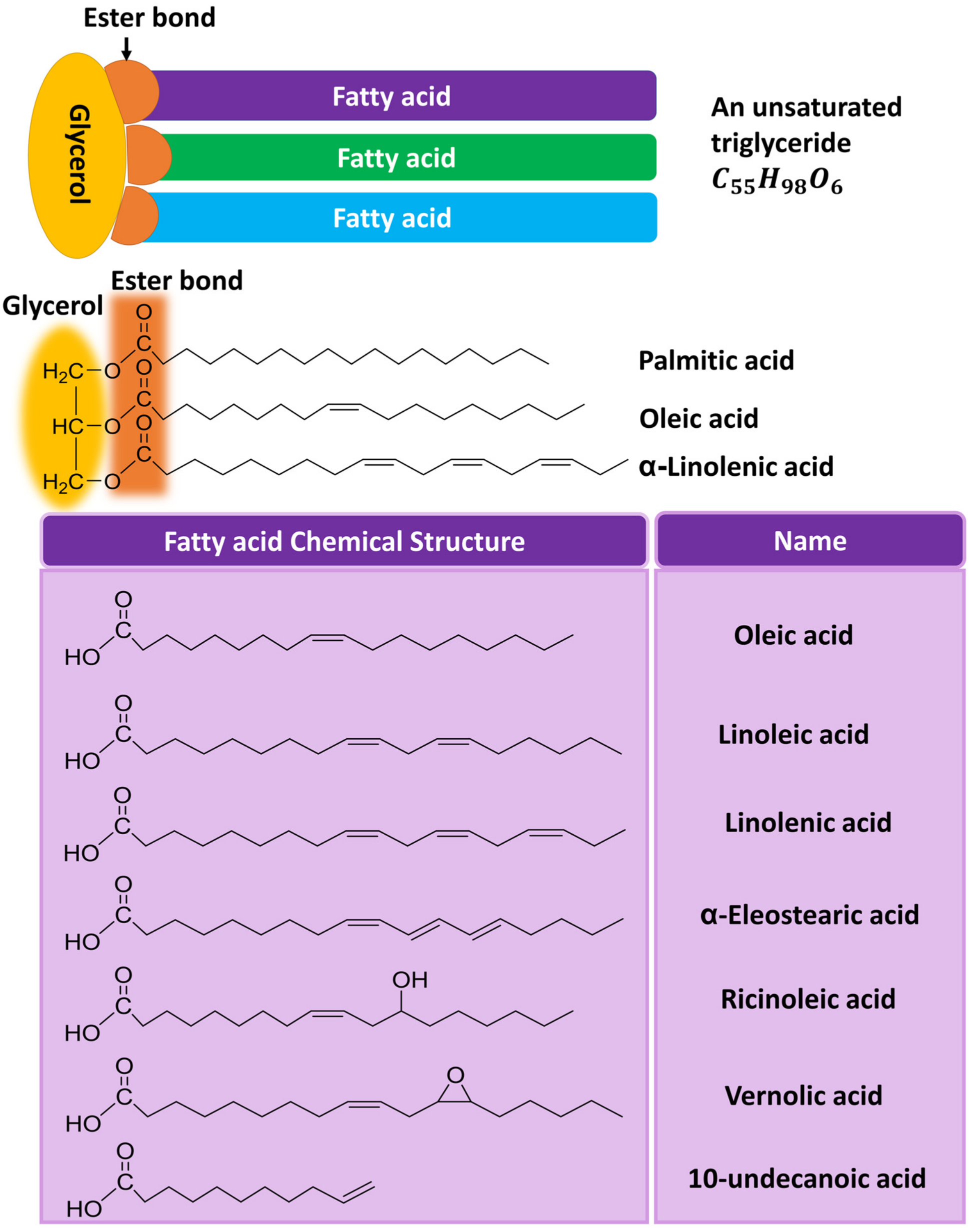

Fig. 6 (Top) Example of an unsaturated triglyceride in vegetable oils, which is composed of glycerol and fatty acids (figure on the top is redrawn from ref. 69 with kind permission of the website owner). (Bottom) Chemical structure of some common fatty acids (figure on the bottom is redrawn by the authors in ChemDraw from ref. 70 with kind permission from RSC, copyright 2010).

including denaturation, additive blending or crosslinking in natural polymers can influence their ultimate biodegradability. The biodegradability test revealed that the denatured whey protein within plasticizer degraded quickly even after applying it to the commercial PLA film (*i.e.*, fully mineralized during 20 days of the test performed in liquid medium).[82] Modification of whey protein isolate (WPI) with montmorillonite nanoplatelets and plasticizer (glycerol or sorbitol) produced WPI-based nanocomposite coatings with improved barrier against oxygen permeation, while the elongation was reduced.[83]

Rocca-Smith *et al.*[42] boosted the barrier properties of PLA against water vapor and oxygen by developing a wheat gluten (WG)-based multilayer system, PLA-WG-PLA (Fig. 8a and b). Moreover, WG coating thickness had a non-linear relationship with oxygen permeation (OP) (Fig. 8c), showing an exponential decrease for thicknesses below 10–20 μm. The compatibility of PLA and WG layers in the fabrication of multilayers was improved by hot pressing as well as a corona treatment. The interface adhesion between layers is defined as the work of adhesion (W_a), which has determined values according to the applications (Table 2). In a similar study using PLA-WG-PLA laminate with hot-pressing, Cho *et al.*[84] obtained W_a values that were 2 orders of magnitude higher. However, they prepared WG layers without using solvent as opposed to Rocca-Smith *et al.*[42]

Table 1 Summary of lipid-based coatings

Lipid-based coating and substrate	Modifications	Coating method	%Barrier improvement WVP/WVTR/OP	Ref.
Whey protein isolate-cellulose film-coated beeswax for coating on paperboard	Using glutaraldehyde as crosslinking agent and glycerol as plasticizer	Melt-brush coating and heating compression	92–95% reduction in WVTR	60
Beeswax-ethyl alcohol emulsion-coated trays of thermoplastic starch/polylactic acid	Using Tween 80 as emulsifier	Immersion coating	97.46% reduction in WVP	61
Crosslinked chitosan/beeswax layer-coated PLA film	Corona treatment of PLA surface, crosslinked chitosan with sodium tripolyphosphate prior to beeswax coating	Coating applicator and hot melt roll coater	100% reduction in WVTR 23.77% reduction in OTR	62
Hydroxypropyl methylcellulose incorporated with beeswax-coated plums	Using glycerol as plasticizer	Immersion coating	20–50% reduction in WVP Improved shelf life of plums	63
Silylated soybean oil-coated paper	Silane treatment of soybean oil by vinyltrimethoxysilane	Laboratory roll-lab coater	53.1% reduction in WVTR	74
Cassava starch incorporated with beeswax-coated guavas	Using saponificated sunflower oil as surfactant (emulsion former of coating solution)	Immersion coating	39% reduction in WVTR Improved shelf life of guavas	75
Cinnamaldehyde-incorporated natural plant poly phenol coating	—	Dip-coating	Antibacterial properties	77
Epoxidized soybean oil and ZnO nanoparticle-coated paper/fabric	Epoxidized soybean oil cured with sebacic acid as adhesive component, using stearic acid as low energy modifier	Dip-coating	Reduced wettability and high hydrophobicity	78

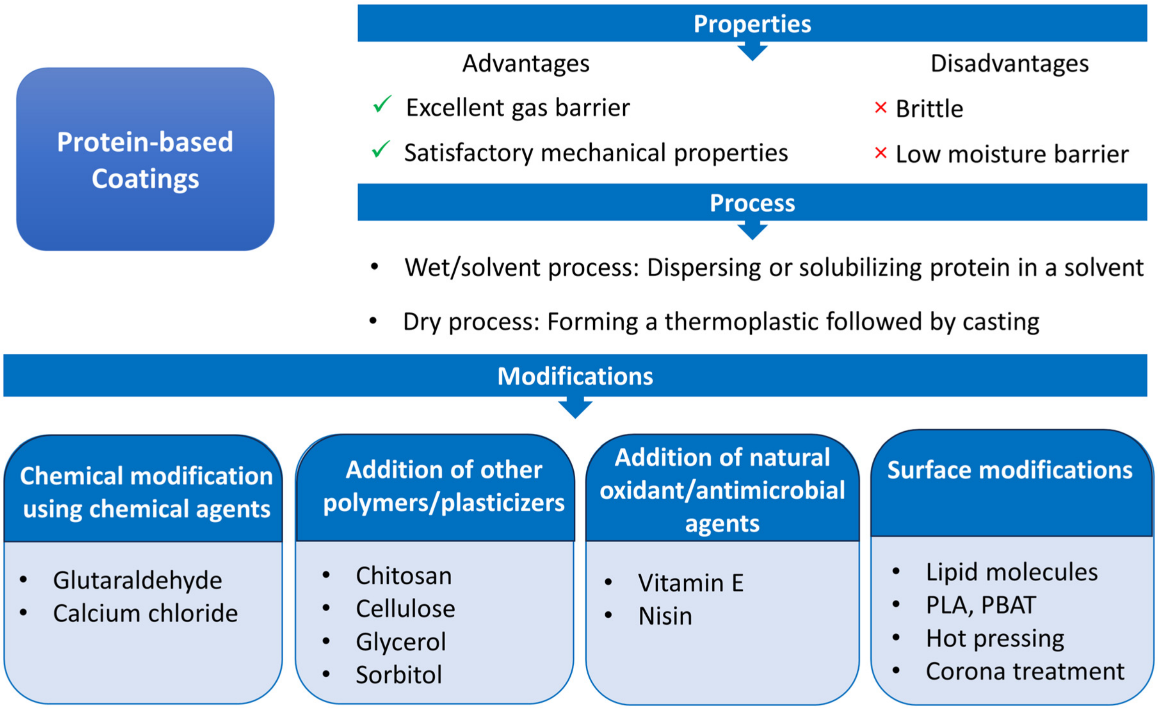

Fig. 7 Protein-based coatings, their properties and common processes as well as strategies for modification of proteins to improve their performance.

This was explained by a hypothesis on evaporation of residual solvent, which could have an adverse consequence on the compatibility and adhesion of PLA and WG layers.

Zein and gelatin have been also extensively used for developing biodegradable coatings. Zein's features include plasticity, heat sealability, biodegradability[13] and intrinsic hydro-

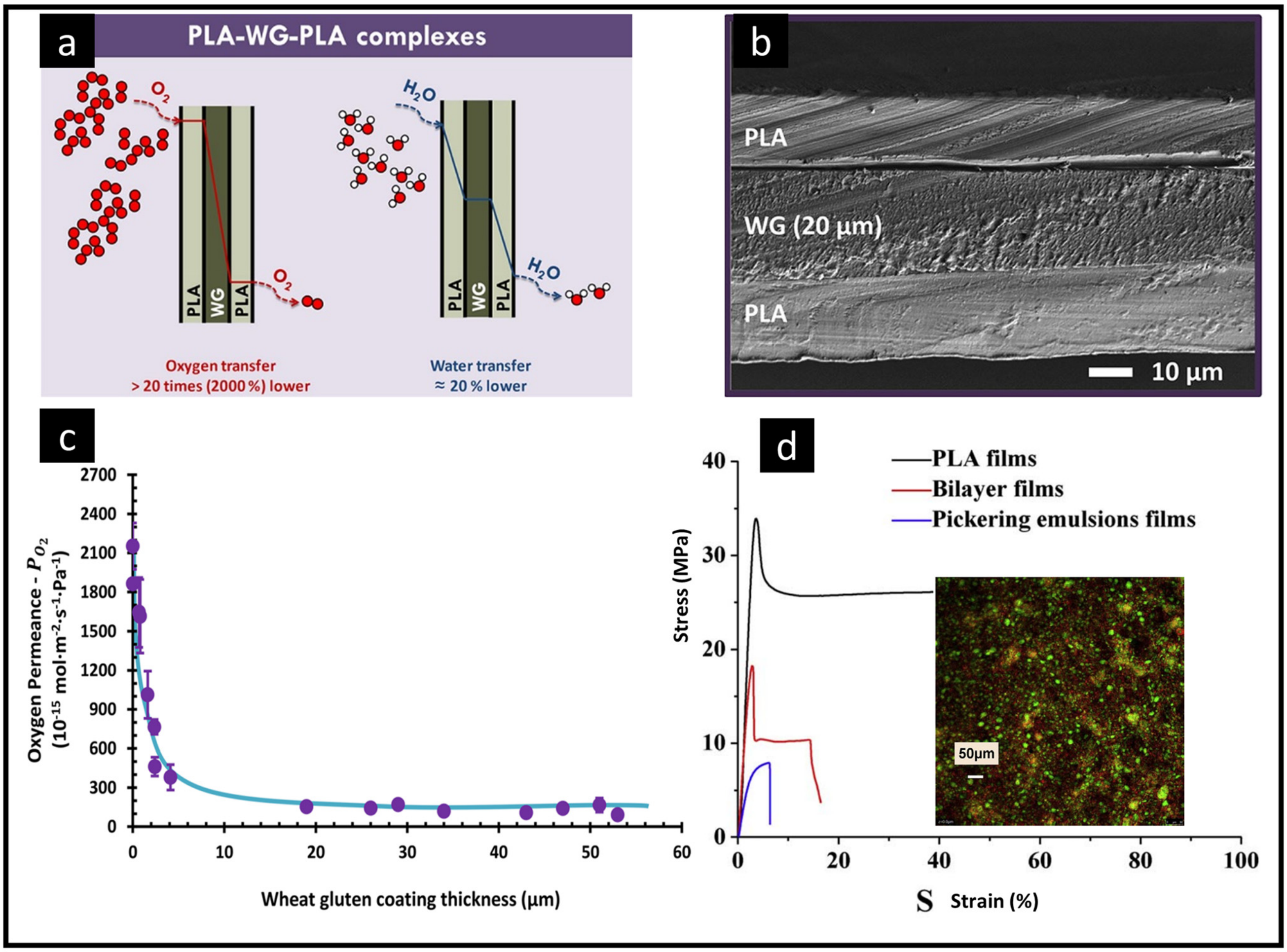

Fig. 8 (a) Schematic of multilayer laminate PLA/wheat gluten (WG)/PLA and representative resistance against oxygen and water vapor permeation, (b) the cross-section SEM image of multilayer laminate with total thickness of 60 μm, in which WG is 20 μm, (c) OP of multilayers *versus* WG coating thickness (figure a–c are reproduced from ref. 42 with kind permission from ACS, copyright 2019, open access). (d) Stress–strain curve of PLA, bilayers and Pickering emulsion films as well as confocal laser scanning microscopy (CLSM) of Pickering emulsion films (selective exciting either Nile blue A (red, zein) or Nile red (green, oil) was used to take the micrographs), reproduced from ref. 89 with kind permission from Elsevier, copyright 2018.

Table 2 Theoretical work of adhesion for some of the industry film/coating applications. Data are reported from ref. 90

Industry application	Theoretical work of adhesion value (W_a)
Latex painting applications to surfaces	More than 70 mN m^{-1}
Organic applications to metals	Around 65 mN m^{-1}
Printing paper and polymer films	60 mN m^{-1}

phobicity due to a high content of nonpolar amino acids.[85] Therefore, it can be a better moisture barrier than other protein-based biopolymers.[13] Although zein-based films are reported to have great stability in high humidity and heat, they show high solubility and weak mechanical properties compared to other proteins like gluten and fish protein.[85] Zein fibers loaded with phenolic-rich orange chilto extracts were electrospin-coated on PHA films followed by chemical modification of the surface with glutaraldehyde vapor as a cross-linker. The water resistance of PHA-coated films significantly improved, and crosslinked zein fibers maintained their fibrous structure after 12 days of immersion in water.[86] The intrinsic hydrophilicity of gelatin has restricted its application in food packaging.[87] Laminating gelatin with other polymers was reported to address this issue.[87,88] Fish gelatin was used to develop multilayers of PLA/fish gelatin/PLA with improved oxygen barrier properties compared with neat PLA. The PLA surface was modified by corona discharge to improve the interface adhesion between layers. Fish gelatin was modified using glycerol reinforced with CNC and antioxidant extract from almond shell by-products. Hydrogen and covalent bonding between the antioxidant and gelatin improved the ductility.[87] In similar work, fish gelatin's water vapor permeability was reduced by developing multilayers of PLA/fish gelatin/PBAT.[88]

Zhu *et al.*[89] took the advantage of both proteins and polysaccharide to develop a Pickering emulsion of zein–chitosan complex suspension mixed with maize germ oil, which was then coated onto a PLA film. The miscible properties and interface interaction of chitosan and PLA (zein/chitosan complex particles) was responsible for the increased strength and extensibility of bilayer films compared with emulsion films (Fig. 8d). The oil was evenly distributed and filled throughout the zein–chitosan network matrix, according to fluorescence laser scanning microscopy (Fig. 8d). Water vapor permeation (WVP) was 1–2 orders of magnitude smaller than films from only biopolymers (*e.g.*, soy-protein isolate, chitosan films) and the protection against OP also improved.[89]

Overall, coatings based on proteins exhibit a good oxygen barrier as well as medium mechanical behaviour. However, their sensitivity to water restricts their applications. Physical or chemical post-treatment techniques can be used to improve protein properties for coating applications. A summary of protein-based coatings is presented in Table 3.

3.1.3 Polysaccharide-based coatings and derivatives

3.1.3.1 General overview of polysaccharide-based coatings. Starch and its derivatives, cellulose derivatives, alginate, pectin, chitosan, and carrageenan are polysaccharides utilised in edible coating compositions[71,91] (Fig. 4). Alginate and carrageenan can be applied as rather thick coatings on the surface of food to avoid moisture loss. As a result, until the coating dehydrates, the food does not lose significant moisture.[81] Cellulose, starch, chitosan, alginate and pectin are the main polysaccharide-based materials for biodegradable coating applications.

At low relative humidity, polysaccharides provide an effective barrier to gases like carbon dioxide and oxygen, which lies behind their packed network structure of hydrogen-bonding. However, their hydrophilic nature causes them to have a poor moisture barrier property.[71,81,92] On the other hand, polysaccharides are rigid and brittle polymers. For example, the tensile strength of a film of chitosan or amylose starch can be compared with other films based on HDPE. The main concerns are flexibility and elongation, which are far less than those of synthetic polymers. The way this issue has been addressed in the literature is to combine polysaccharides with other biopolymers.[93] The efficiency and functional behavior of polysaccharide-based coatings depend on the use of plasticizers, relative humidity, casting solvents, and the pH level.[93,94]

Using the LBL coating process, multilayer films (total of 30 layers with final thickness of 4 μm) were created from sodium alginate/polyethyleneimine (ALG/PEI) on biaxially oriented PLA films by Gu *et al.*[95] (Fig. 9a and b). The OTR was 1.22 cm^3 $(\text{m}^2\ \text{d atm})^{-1}$ and OP was less than 3.8×10^{-17} $\text{cm}^3\ \text{cm/cm}^2$ s Pa. The latter was three orders of magnitude less than the BioPLA film. By increasing the number of coated layers, both tensile strength and elongation slightly increased as the coating layers are too thin to have a significant effect on the BioPLA film.[95] Likewise, Dai *et al.*[96] developed a transparent multilayer film based on cationic guar gum (CGG) and TEMPO-mediated oxidised cellulose nanofibrils (TOCNs) using the LBL solution coating. The multilayer films showed WVTR as low as 68.52 g $(\text{m}^2\ \text{d atm})^{-1}$ and OTR of 5.56 cm^3 $(\text{m}^2\ \text{d atm})^{-1}$ and resistance to canola dyed oil (Fig. 9c–e). The LBL coating method has the advantage of electrostatic attraction between anion and cation and intermolecular hydrogen bonding, which densify the film structure and enhance the mechanical and barrier properties.[96] Cellulose nanocrystals containing citric acid was developed as a biodegradable coating, in which the addition of up to 20% (by weight) citric acid to CNC resulted in improved WVTR compared with neat CNC. The improved WVTR occurred due to filling of free volumes in the coating matrix as well as citric acid's higher hydrophobicity.[97]

Starch and derivatives of starch (*e.g.*, hydroxypropylated high amylose starch and amylose starch) have a reputation for being a low-cost packaging material, with great film-forming capabilities and high water solubility.[98,99] The mechanical strength, flexi-

Table 3 Summary of protein-based coatings

Protein-based coatings and substrates	Modifications	Coating method	%Barrier improvement WVP/WVTR/OP	Ref.
Whey protein-coated PLA	Addition of sorbitol	Control coater	OP reduced by 84%	82
Whey protein isolate-coated PET	Addition of montmorillonite and glycerol or sorbitol	Wired rod	OP reduced by 91% for glycerol-plasticized and 84% for sorbitol plasticized	83
PLA-WG-PLA multilayers	Addition of glycerol, high-pressure homogenization and corona treatment	1. Wet casting or spin-coating 2. Hot pressing	OP reduced by 2000%, WVP reduced by 20%	42
PLA-WG-PLA multilayers	Addition of glycerol	Hot pressing	OP reduced by 99%, WVTR reduced by 54%	84
Zein fibers loaded with orange chilto extracts-coated PHA	Addition of glutaraldehyde as crosslinker and hot pressing	Electrospinning	Improved water resistance	86
Zein–chitosan Pickering emulsion and maize germ oil-coated PLA		Casting	WVP increased by 63%, OP reduced by 94%	89
Fish gelatin + CNC coated PLA	Corona discharge and addition of CNC and antioxidant to fish gelatin	Laminating with thermo-compression	OP reduced by 78%	87
PLA/fish gelatin/PBAT	Addition of glycerol	Wet casting	WVP reduced by 42%, reduced water solubility	88

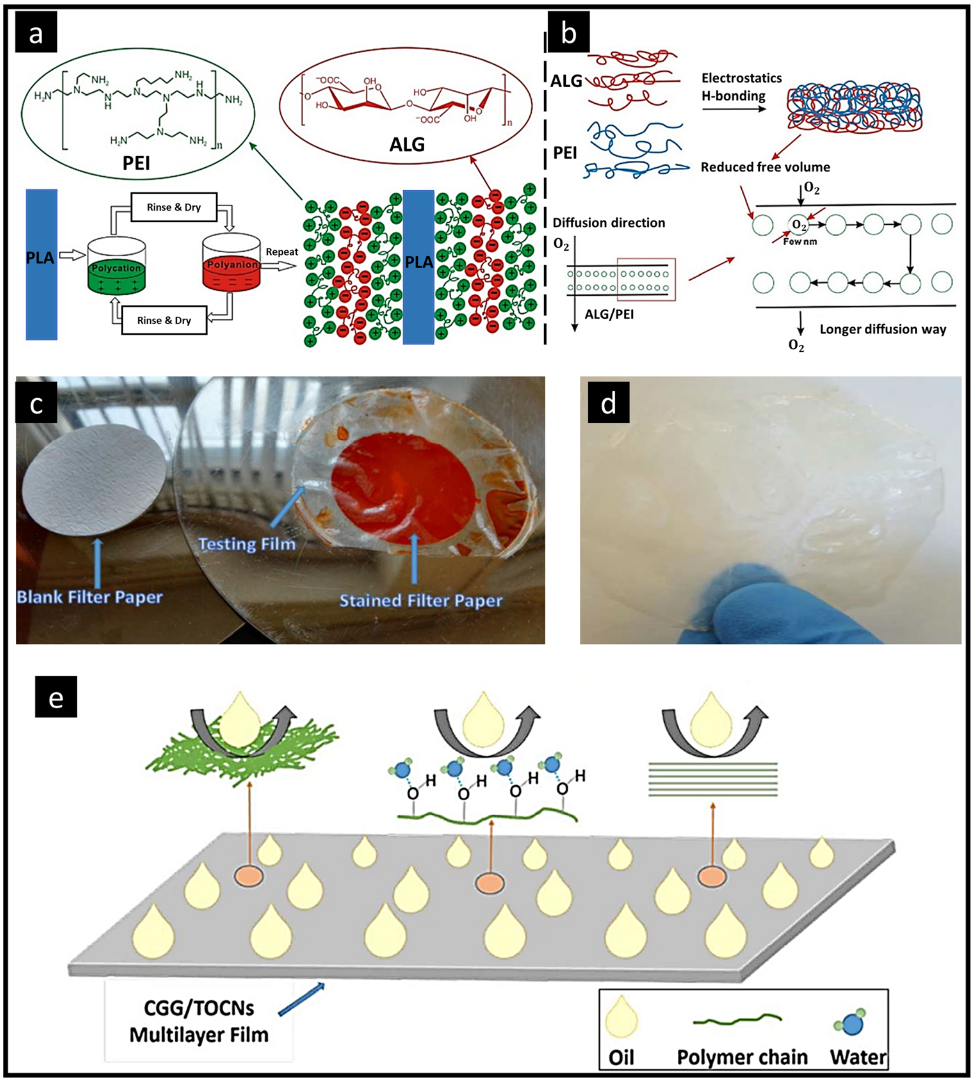

Fig. 9 (a) LBL coating process in multilayer structure of ALG/PEI on BioPLA films. (b) A schematic of the multilayer film's reduced free volume due to strongly interdiffused ALG/PEI layers through electrostatic H-bonding, interpenetration and tangling of polymer chains. Therefore, the channel for O_2 diffusion *via* the layers was lengthened, contributed to better oxygen barrier of the films (figure a and b are reproduced from ref. 95 with kind permission from Elsevier, copyright 2013). (c) and (d) A sandwiched structure including "saturated filter paper with canola dyed oil-film sample-blank filter paper" was used for oil resistance test in CGG/TOCNs multilayer films and showed no discoloration. (e) The mechanism of oil-resistance in multilayer films (figure c–e are reproduced from ref. 96 with kind permission from ACS, copyright 2017, open access).

bility, and transparency of starch-based films are impressive. However, they have high WVTR, which might alter the inside environment of the package, favoring microbe development and resulting in product weight loss.[99,100] Some other notable works have also been done on the utilization of thermoplastic starch in various forms and combination of those with biodegradable polyesters[101–103] and alginate[104] as well as proteins.[105]

In food applications, the most widely used cellulose derivative is carboxy methyl cellulose (CMC).[106] To create a barrier against oxygen, moisture, and oil transfer, edible coatings made from CMC, hydroxy propyl cellulose (HPC), methyl cellulose (MC), and hydroxy propyl methyl cellulose (HPMC) have been used for vegetables and fruits.[71] Among these, CMC is the most applied coating for maintaining the crispness and firmness of fruits including apples, peaches, berries, carrots, celery, and lettuce.[71,107] Additionally, CMC helps to preserve the flavour of fresh fruits and vegetables.[71] This is achieved through the simulation of a regulated atmosphere, in which the oxygen uptake is reduced without any increase in carbon dioxide amount in the internal environment of coated apples and pears.[71]

Chitosan is one of the most efficient materials for coating fresh produce because of its great film-forming property and adaptability with minerals, vitamins, and antimicrobial agents.[108] Fruits that are highly perishable (*e.g.*, strawberries, grapes, raspberries, mango) have been coated with chitosan-based coatings to protect from fungal decay.[108] Chitosan coatings combined with nanoemulsions have been studied for their bactericidal activity. For example, mandarin essential oil has been loaded as nanoemulsion into chitosan coatings to protect green beans against *Listeria innocua* through the application of UV-C, ozonated water treatments and γ-irradiation to enhance the antibacterial effect up to 3.3 log CFU per g. Although the bioactive coating combined with γ-irradiation produced a synergistic and steady antibacterial impact with no negative effects on colour over the storage time, the reduction in sample firmness was a drawback. To overcome this problem, the combination of UV-C with bioactive packaging is a solution to avoid reducing the firmness during storage time.[109] Oil and water-repellent paper coatings were developed by the rod-coating of chitosan solution followed by further modification of the paper surface with polydimethylsiloxane (PDMS). Coated papers showed maximum fat resistance (kit value of 12/12) and great water resistance (WCA of 95.2°).[110]

Although polysaccharides have gained a lot of attention in multilayer food packaging, there is not a clear approach to decide in which layer of bio-based multilayer packaging materials polysaccharides should be used (*i.e.*, outer or inner layer, facing-air layer, intermediate layer).[81] Another noteworthy point for polysaccharide-based coatings is regarding those derived from xylans and mannans, which have shown low permeability of oxygen and grease as well as good tensile strength.[111] Therefore, biopolymer blending and laminating using xylan/mannan can be used to develop novel multilayer composites.

3.1.3.2 Nanocellulose and nanochitin-based coatings. Cellulose and chitin are the first and second most abundant polysaccharides[112] and exhibit beneficial properties such as renewability, biodegradability and high crystallinity.[113]

The chemical structure of chitin closely resembles that of cellulose, with the key distinction being the presence of acetamide groups in chitin, as opposed to the hydroxyl groups found in cellulose.[114] In the past few years, there has been a significant surge in research projects focused on nano-scaled cellulose. Concurrently, there has been a growing interest in the isolation and extraction of nanosized crystalline chitin, known as chitin nanocrystals or whiskers.[114]

Cellulose-based nanoparticles are known as nanocellulose, characterized by having at least one dimension measuring less than 100 nm and length extending to several micrometers. Nanocellulose can be extracted from bio-sources like wood, hemp, linen, flax, tunicates and algae, and exists in three forms, namely nanocrystalline cellulose, nanofibrillated cellulose and bacterial nanocellulose.[115] Common nanostructures for chitin are in the form of nanofibrillar composites, nanofibers and nanowhiskers/nanocrystals, and can be extracted from mushrooms and shellfish as well as the mineralized structure of diatoms and sponges.[114]

PLA coated with multilayers of cationic chitin nanofiber and anionic cellulose nanocrystals (CNC) using layer-by-layer spray coating improved the oxygen barrier properties of the final composite films by 73%. PLA coated solely with chitin nanofiber or CNC exhibited greater O_2 permeability and haze compared with PLA coated with multiple layers of both chitin nanofiber and CNC. By increasing the coating thickness for 5 layers of chitosan nanofiber/CNC-coated PLA, a mutual interlayer destruction caused a sharp decrease in ultimate tensile strength and breaking strength.[116] In a similar study, PLA-coated nanocellulose/nanochitin using layer-by-layer assembly improved the hydrolysis resistance, which avoided loss of molecular weight and tensile strength. Nanocellulose/nanochitin coating reduced the water contact angle (from ∼87° for neat PLA to ∼65° for coated PLA) due to increased hydrophilicity, but further treatment with microwave irradiation increased the water contact angle to ∼70° and prevented the coating layers from peeling off the substrate.[113]

Flexible, transparent and gas impermeable coatings have been based on cellulose nanofibers (CNFs) and chitin nano whiskers (CNWs) spray-coated in a layer-by-layer assembly method on a PET substrate. The oxygen barrier of the multilayer $(CNF/CNW)_{20}$ improved significantly (more than ∼65%) compared with single layers of CNF or CNW. Further treatment of PET-coated CNF/CNW through hot-pressing reduced the OTR by ∼27%.[117] In a similar study, the layer-by-layer coating technique was used to coat nanocellulose/nanochitin on polypropylene films. A 20-layer coating of nanocellulose/nanochitin with a total thickness of 60 μm decreased the OTR by ∼98% (from 1118 to 13 cc per m^2 per day) due to the high crystallinity of nanochitin and nanocellulose.[118] It is important to note that further investigation of biodegradability for these types of multilayers is needed to ensure that the biodegradability of the coating alone is not disrupted after coating on a petro-based non biodegradable polymer such as PET or PP.

Thermal treatment has produced significant improvement in the case of nanochitin and nanocellulose coatings on cellulose acetate substrate. In a study, the spray-coated nanochitin/nanocellulose films were optimized in terms of spray coating temperature and thermal post-treatment temperature. By raising the spray temperature (from 40 to 100 °C) and the thermal temperature (from 40 to 140 °C), the OP reduced by 48% and 62%, respectively, reaching the optimal OP of 11.5 cm^3 μm m^{-2} day^{-1} kPa^{-1}, which is comparable to oriented PET. The mechanical properties and WVP of the coated films exhibited an average enhancement of 20% and 11%, respectively, compared with neat cellulose acetate, with no significant influence observed from the temperatures.[119]

The cellulose nanocrystal Pickering emulsion has been integrated into chitosan coatings to increase hydrophobicity on pears during extended periods of cold storage. At 83% relative humidity (RH), the ethylene production in commercial Semperfresh™ coating and chitosan-reinforced CNC coated fruit tended to rise compared with those at 43% RH due to increased water absorption into the coating and reduced hydrophobicity. Conversely, fruit coated with Pickering emulsion CNC incorporating chitosan stored at 83% RH exhibited no significant increase in ethylene production compared with those stored at 43% RH. This indicates the greater hydrophobicity and stability at high RH of these coatings, effectively suppressing ethylene production, thereby delaying fruit ripening.[120]

Cellulose nanofiber and nanocrystal (CNC) coatings have demonstrated a reduction in the oxygen transmission rate (OTR) of the treated substrate.[121,122] It is noteworthy, however, that the majority of studies have focused on self-standing cellulose films (fibers and/or crystals) or coatings applied to polymeric substrates, as reviewed above, but a few studies are focused on porous substrate such as paper/paperboard.[122,123]

Cellulose nanocrystals were applied to paper with small (0.45 μm) and large (11 μm) pores using a layer-by-layer method involving spinning and dipping. The paper with large pores, coated with 10 layers of CNC (23 μm thickness), exhibited the highest water contact angle WCA of 73°. The CNC coating demonstrated low oxygen permeability, ranging from 0.12 to 24 mL μm $(m^2\ 24\ h\ kPa)^{-1}$, at 23% relative humidity (RH). At 50% RH, the oxygen permeability (OP) was too high to measure, except for the dip-coated sample (with a thickness of 23 μm), which exhibited an OP of 6.2 mL μm $(m^2\ 24\ h\ kPa)^{-1}$ – lower than that of LDPE, PET, and PS. However, extended storage led to a decrease in OP, indicating a weakening of the coating's barrier properties over time.[122]

A novel multilayer was developed by coating of CNC/CNW on one side of PET, and silica nanoparticles/CNW coated on the other side. The former side was treated with hot-pressing and the latter side was impregnated with sunflower oil with self-cleaning properties, and showed WVTR of 1.4 g m^{-2} day^{-1}. The multilayer showed the WCA of maximum 154° with significant oxygen barrier properties of 0.1 mL per m^2 per day.[124] In another study, the CNW-CNC coating, in which CNW was treated by aggressive deacetylation, demonstrated an approximate ∼20% decrease in the WVTR compared with uncoated cellulose acetate (CA) films by experiencing only a marginal ∼10% reduction in ultimate tensile strength and no noteworthy decline in failure strain. Multilayer films were achieved with a substantial 91–99% decrease in oxygen permeability (OP) as a result of tuning chitosan deacetylation, compared with uncoated CA films.[125] Interestingly, a non-acidic chitosan coating technique was developed for preparing all-natural, biodegradable, and water-resistant paper coating. Filter paper coated with CNW and soybean oil improved the WCA to more than 90° at zero time and water absorption of less than 10% at 5 min.[126]

Reviewing the applications of nanochitin and nanocellulose coatings, it becomes apparent that utilizing these materials as polysaccharide-based substances can be considered as a sustainable alternative in packaging applications.

Throughout section 3.1, we reviewed coatings from nature including lipid, protein, and polysaccharide-based coatings. Critical barrier properties and functions of edible coatings from natural sources for fresh vegetables and fruits are summarized in Fig. 10. Coatings should have low permeability to water vapor to reduce the rate of desiccation and maintain the crunchy surface of the food. In addition, they should have a low O_2 permeability to reduce rate of respiration. However, O_2 permeability should not be too low to avoid anaerobic conditions, production of ethanol, and off-flavor. Moreover, oxidation rates of the food can be reduced by barrier coatings against UV light.[127] Coatings can serve as a frying oil barrier, so that the final oil content of the fried food remains low. Finally, coatings have the capability to impart additional characteristics to the food such as a shiny and smooth surface, as well as providing antimicrobial and antioxidant properties. All these contribute to extending the shelf life of food.[128]

3.1.4 Biomass and agriculture waste-based coatings. Packaging coatings/films should include at least two components: a matrix (*i.e.*, a macromolecule) that provides the

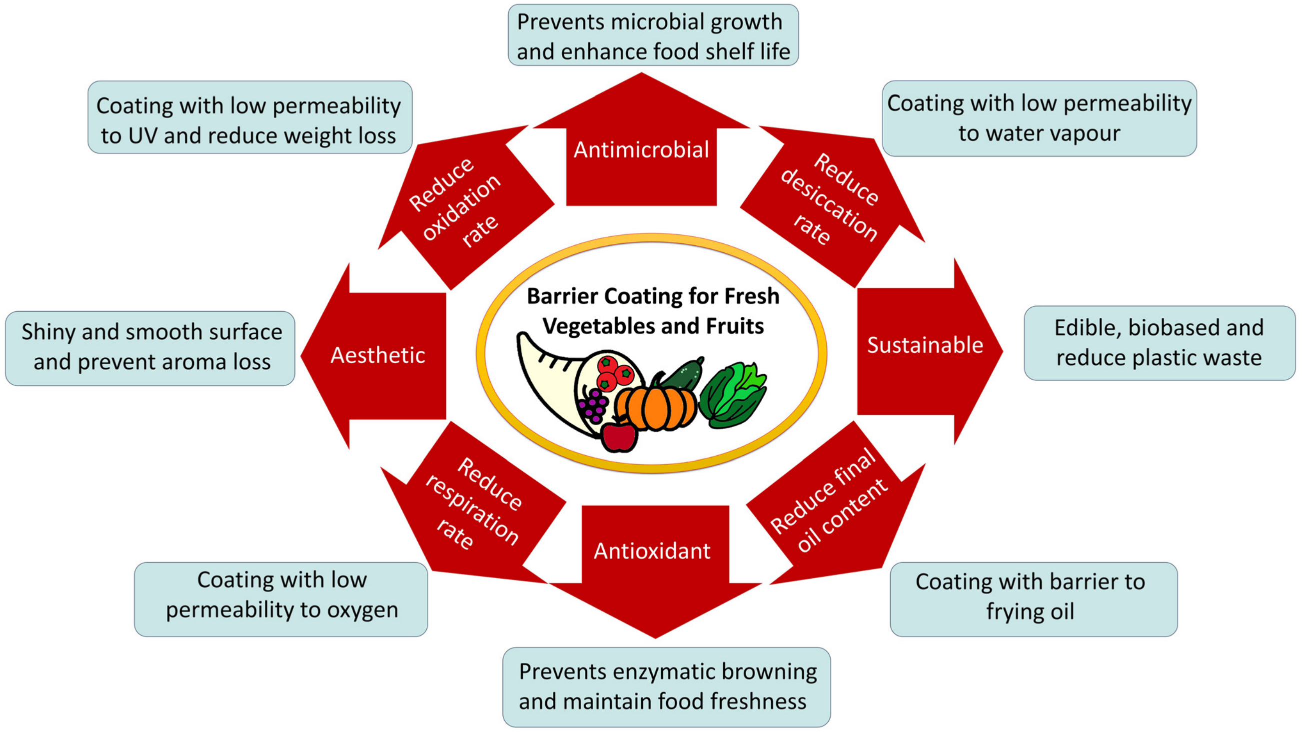

Fig. 10 Critical barrier properties and functions of an edible coating for fresh vegetables and fruits. The figure is drawn by the authors based on contents in ref. 127 and 128.

cohesive structure, and a plasticizer to reduce brittleness and rigidity. Other materials can also be added to coatings/films to increase their physical, mechanical, and barrier characteristics[127] (Fig. 11).

Biomass and agriculture waste, as renewable biorefinery feedstocks, have also been used to develop coatings.[127,129] There are three generations of biorefineries, where the raw material is a feedstock obtained from a crop such as maize, corn, sugar beet, cassava and sugarcane (1st generation), cellulosic residue, forestry waste and agro-industrial waste (2nd generation), and microalgae, CO_2 capture and utilization (3rd generation).[130,131] Food waste is rich in carbohydrates, proteins or lipids and therefore is a potential source of biopolymers.[132] Fig. 4 shows the main types of biopolymers that can be achieved from agricultural waste. For example, gelatin can be obtained from slaughterhouse wastes, which contain good sources of protein from animal origins.[51] Gluten is a protein naturally found in some grains such as wheat and barley as a by-product of wheat starch production.[133] Lipid biopolymers could be obtained from natural sources like cutin extraction from tomato by-products.[134,135] Polysaccharide biopolymers such as pectin can be obtained from peels and seeds of different citrus fruits (mango, banana, orange) as well as from juice manufacturing by-products[51] and potato or cassava waste peels, which are a rich source of starch production.[136]

Agricultural wastes such as corn straw, rice straw, wheat straw, sugarcane bagasse, and rice husk are the most abundant type of biomass waste.[137] Crop straw is produced from the dry stem or stalk after removing the grain and chaff from the field. The main constituents of crop straw are cellulose, hemicellulose, and lignin.[138] The shelf life of avocados and fresh eggs has been extended through immersion coating in cellulose derivatives.[139,140] Hemicellulose-based coating solutions are used to extend the shelf life of cheese by chemically modifying chitosan and galactomannan in the presence of a plasticizer and corn oil.[141] Pectin has been used for applications in food packaging as a coating on cut and fresh fruits or vegetables as well as in microencapsulating materials, with antioxidant and antimicrobial properties.[51] In addition, pectin coatings can be used in minimizing ripening and post-harvest rottenness, as well as enhancing tomatoes sensory characteristics.[142] Modifying the atmosphere around the fruit through applying a pectin-based coating impacts the oxygen level and avoids ethylene production. Therefore, the physiological decay of the fruit will be postponed. Moreover, pectin was mixed with corn flour to make a coating solution on fresh tomatoes and resulted in the formation of hydrophobic regions.[142]

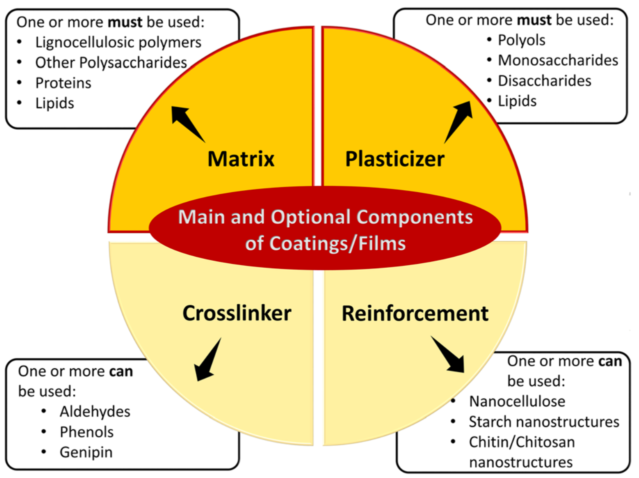

Fig. 11 Films and coatings derived from biomass should contain at least two components: matrix (consist of a macromolecule that makes the cohesive structure) and plasticizer (reduce brittleness and rigidity). Other optional components are crosslinker and reinforcement to improve physical characteristics of films/coatings. Some examples are shown for each component in the boxes. Figure has been redrawn by the authors from ref. 127 with kind permission from Elsevier, copyright 2014.

Among different biopolymers from by-products of the food industry, fruit and vegetable residues are typically processed into flour and have shown remarkable promise for flexible film/coating applications without the addition of plasticizers. Andrade *et al.*[143] created novel edible bilayers from flour that are produced from a variety of residues (orange, watermelon, lettuce, carrot, spinach, mint, and cucumber) using the casting method. Furthermore, the incorporation of flour made from the residue of potato skin enhanced the tensile strength. The high content of carbohydrates in potato skin resulted in high flexibility but lower strength in comparison with films made from fruit starch. The WVP values for the films made in this study were lower than those found in films made from banana puree ($3.03\ \mathrm{g\ mm\ m^{-2}\ h^{-1}\ kPa^{-1}}$)[144] but comparable to those found in films made from mango puree ($2.66\ \mathrm{g\ mm\ m^{-2}\ h^{-1}\ kPa^{-1}}$).[145]

Abundant plant cell wall polysaccharides, namely xylan and mannan, can be produced from by-products of the forestry and agriculture industry.[111] Edible coatings based on xylan and mannan were tested on fruits.[146,147] Apples coated with arabinoxylan and β-glucan stearic acid ester showed reduced weight loss and improved shelf life during storage time of more than 30 days.[147] Mikkonen *et al.*[111] reported that coatings derived from xylan's and mannan's biorefinery products have oxygen barrier properties comparable to that of EVOH. In addition, their mechanical strength was also comparable to petro-based materials, though their stretchability was much lower. Further studies are needed for the evaluation of safety and quality of wastes derived from agricultural products. Moreover, practical, and cost-effective ways for converting wastes from biomass to raw materials should be developed to allow industrial mass manufacturing.[138]

3.2 Polyester-based coatings

3.2.1 Synthetic petroleum-based biodegradable polyester coatings. In this section multilayer structures derived from synthetic oil-based biodegradable materials, such as PCL, PBS and PBAT, are summarized. Currently, PCL and PBAT are the most common synthetic biodegradable polymers that are used in the fabrication of multilayers.

PCL and PBS are thermoplastic polyesters, which are synthesized by a condensation reaction.[148] The melt transesterification and melt polycondensation processes of poly(butylene adipate) (PBA) and poly(butylene terephthalate) (PBT) produce PBAT, an aliphatic–aromatic thermoplastic co-polyester.[149] It has the same mechanical and thermal properties of some polyethylenes. Table 4 shows some of the characteristics of these polymers such as the appearance, melting point, solubility in organic solvents, *etc*. All three polymers have an opaque appearance due to their structures, which means they do not allow light to pass through them.[148] PBAT has a higher melting point than PCL and PBS, although PBAT has a poorly crystalline nature compared with PCL and PBS. Although crystallinity makes a polymer strong, it reduces the impact resistance of the polymer, which is a significant characteristic in the application of food packaging.

A review of the literature on multilayers derived from synthetic oil-based biodegradable polymers shows that the modifications include their blending with each other[150,151] or with polymers derived from agriculture.[152] However, less work has been done on laminating these polymers over each other; some of this is reviewed in this section.

Multilayers of PBAT-coated PBAT/thermoplastic starch (TPS) blend and PBAT-coated PBAT/maleated thermoplastic starch (MTPS) blend showed barrier against oxygen and water vapor.[157] The compression-moulded PBAT/TPS or PBAT/MTPS blend film was dip-coated in PBAT. A rise of 664% and 329% in shear strength was observed for 70TPS/30PBAT-coated PBAT and 70MTPS/30PBAT-coated PBAT, respectively, as compared with the TPS-coated and MTPS-coated films (Fig. 12a and b). This is a result of the fusion of PBAT coating into the blend (Fig. 12c), which allows for MTPS-PBAT covalent bonding and improved layer adhesion shown in SEM (Fig. 12d–g). PBAT coating reduced WVP (59% for PBAT-coated PBAT/TPS and 62% for PBAT-coated PBAT/MTPS), but slightly increased oxygen permeation film (8% for PBAT-coated PBAT/TPS and 25% for PBAT-coated PBAT/MTPS) in comparison with the non-coated blend. Fig. 12h represents the adsorption, desorption, and diffusion of water for these coated films.[157] Cherpinski *et al.*[158] prepared an oxygen-scavenging and water barrier multilayered biopaper by electrospin-coating of polyhydroxybutyrate (PHB) and PCL fibers-containing Pd nanoparticles (PdNP) over the paper. The multilayer was annealed, using a hydraulic press, resulting in a reduction of porosity and an improvement of barrier properties (WVP of 4.3×10^{-11} kg m^{-2} s^{-1} Pa^{-1}) as well as interlayer adhesion. The films of paper/PHB fibers/PCL-PdNP and paper/PHB-PdNP fibers/PCL-PdNP indicated the best performance in oxygen scavenging. In fact, fibers and films from PCL rapidly remove oxygen from head space and are more efficient as a host for PdNP than PHB for oxygen scavenging purposes.[158] Overall, laminating and coating polyesters on each other showed a promising outcome with regards to improving the performance of the final multilayer structure.

3.2.2 Bio-based biodegradable polyester coatings. Herein, we will review multilayer structures available today that have been developed by coating biopolyesters such as PHAs, PLA, PBS, *etc*. on polymeric substrates. Literature reviews show that several studies have concentrated on their blends[159,160] or with other agro-based polymers[161] instead of coating or laminating them with one another. However, effective coating techniques on biopolyesters have been demonstrated, with the main goal of improving their barrier and making them antioxidant or antibacterial for food quality preservation.[81]

For instance, Figueroa-Lopez *et al.*[162] developed PHAs-based active multilayers electrospin-coated with CNC and PHBV active layer containing oregano essential oil (OEO) and ZnONPs (as antibacterial material) (Fig. 13a and b).[162] Multilayers showed an improved barrier against water vapor and D-limonene but the oxygen barrier was not measured due to possible release of essential oil, which could damage the sensor. SEM (Fig. 13c–f) showed that the fibers have a smooth surface with PHBV thickness of ~0.6 μm. Mechanical parameters (tensile strength, modulus, elongation) were reduced in comparison with PHA monolayer due to delamination failure.[162]

Fabra *et al.*[163] studied hydrophobic biopolyesters (*i.e.*, PCL, PLA, and PHB) electrospin-coated on a thermoplastic corn starch (TPCS) film. The main shortcoming of starch-based hydrophilic films is their high sensitivity to water, which results in high plasticization.[163,164] After electrospinning the PCL, PLA, or PHB onto both sides of the TPCS films, the films were heated between hot plates, resulting in continuous and transparent outer layers. The WVP values of TPCS-coated PCL, PLA, and PHB dropped by 83%, 88%, and 91%, respectively. Accordingly, the O_2 barrier of TPCS-coated PCL, PLA, and PHBV was improved by 91% for PCL and PLA and 95% for PHB compared with neat TPCS film.[163,164] Biodegradable aliphatic polyester (PLA, PCL, polyesteramide (PEA), poly(hydroxybutyrate-*co*-valerate) (PHBV) and poly(butylene succinate adipate) (PBSA)) were coated onto plasticized wheat starch

Table 4 Some characteristics of PCL, PBS and PBAT. The table is redrawn by the authors from ref. 148 with kind permission from MDPI, copyright 2021, open access, with added information (for PBAT) and some modifications for PCL and PBS. T_m, λ_c, %, T_g are melting temperature, percentage crystallinity and glass transition temperature, respectively

Polymer	Source	Appearance	Physical property	T_m (°C)	λ_c (%)	T_g (°C)	Ref.
PCL	Oil-based	Opaque	Tough and flexible	70	77	−60	148 and 153
PBS	Oil-based Bio-based	Opaque	Tough and flexible	116	46	−25	148, 154 and 155
PBAT	Oil-based	Opaque	Tough and flexible	120	23	−26	149, 151 and 156

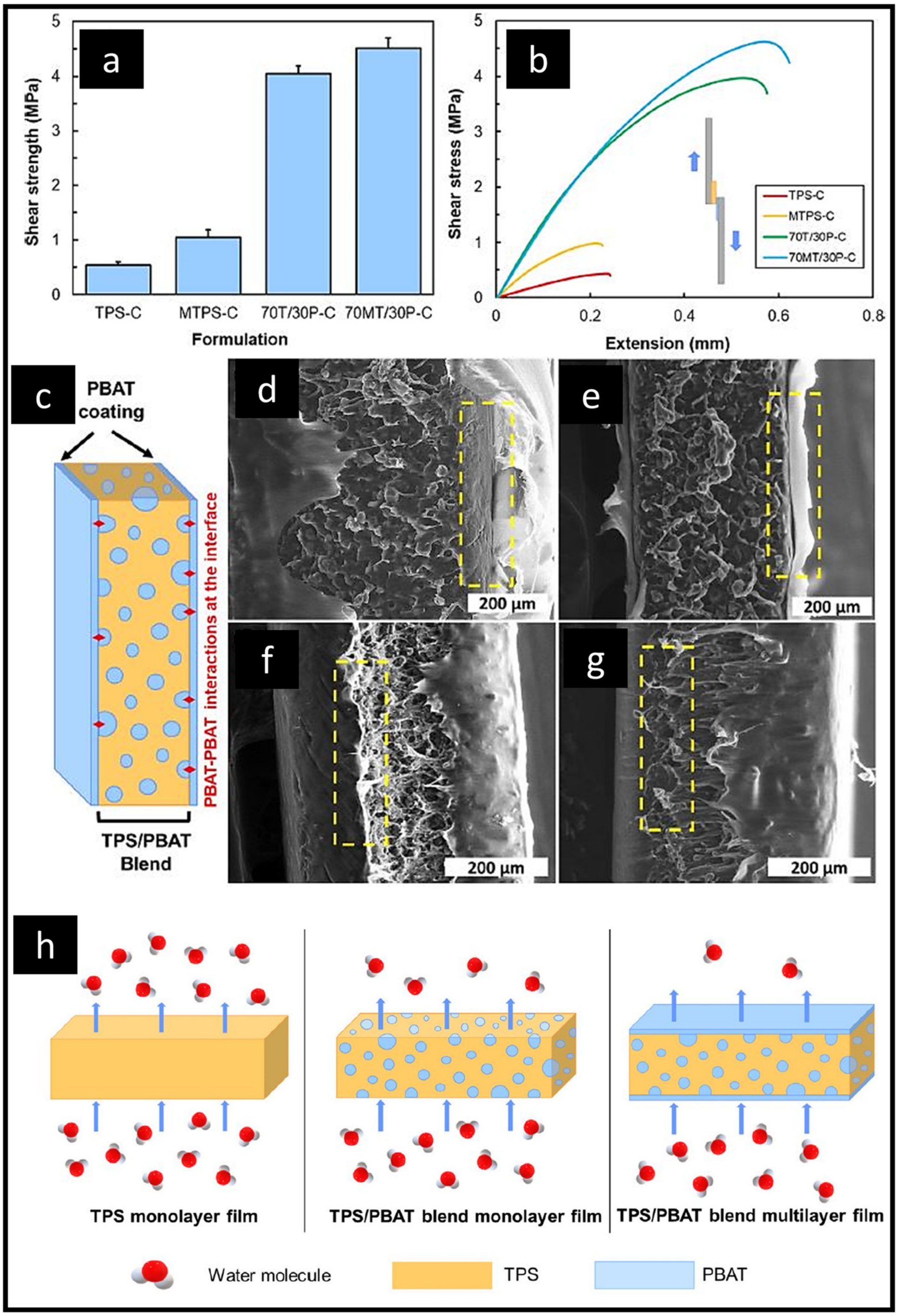

Fig. 12 (a) Interfacial shear strength of PBAT-coated films, (b) multilayers' interfacial shear stress *versus* extension, (c) schematic of TPS/PBAT multilayers; SEM micrographs cross-section of fractured surfaces: (d) MTPS-coated, (e) TPS-coated, (f) 70TPS/30PBAT-coated, (g) 70MTPS/30PBAT-coated films, (h) Schematic diagram of moisture permeation through TPS/PBAT single-layer and multilayer films with PBAT coating. Figure is reproduced from ref. 157 with kind permission from Elsevier, copyright 2021.

(PWS). Polar amide groups in the PEA structure resulted in the high adhesion to the layer of PWS compared to other polyesters. Coextruded films had a substantially higher adhesion (nearly twice) than compression-moulded films. However, the strength of the adhesion varied over time and PHBV layers were peeled away from the starch layer after 50 weeks. PWS/PLA showed the most resistance to moisture and highest hydrophobicity compared with other multilayers.[165]

In a rare study, double-layers of PHBV/PBAT and PHBV/PBSebT (a composite based on PBS) were prepared by co-extru-

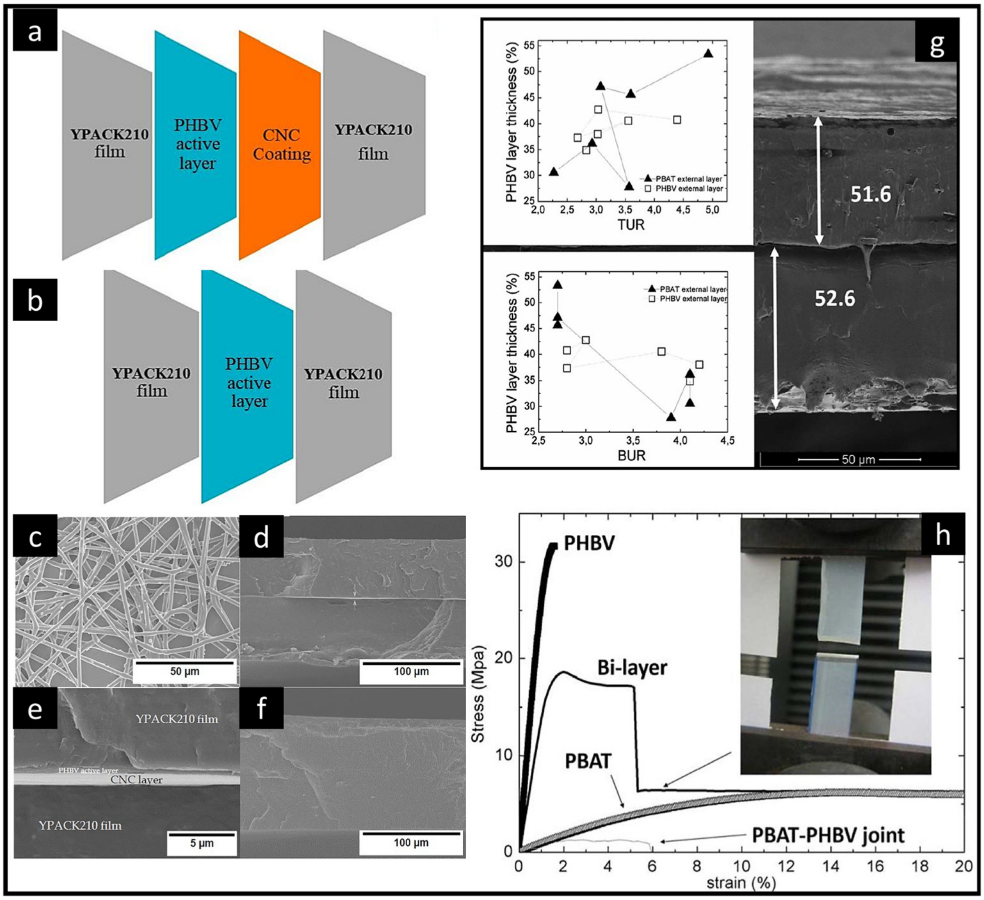

Fig. 13 Schematic figure of active multilayer films, (a) with CNC coating and (b) without CNC coating, scanning electron microscopy (SEM) micrographs of (c) the electrospun fibers of PHBV derived from cheese whey (CW) containing 2.5 wt% OEO + 2.25 wt% ZnONPs and of the active multilayer films (d and e) with cellulose nanocrystal (CNC) coating and (f) without CNC coating (figures a–f are reproduced from ref. 162 with kind permission from MDPI, copyright 2020, open access). (g) SEM image of a bi-layered blown film with blow-up ratio = 2.3 and take-up ratio = 4.1 with an exterior layer of PBAT and (h) stress–strain curves of the double-layered film (with PHBV as the interior layer), PBAT film and PHBV film (figures g and h are reproduced from ref. 166 with kind permission from John Wiley and Sons, copyright 2016).

sion film blowing.[166] Under the same conditions, the thickness variations in co-extrusion film blowing were half that of the blend. Delamination of two layers during SEM sample preparation was evidence of poor adhesion (Fig. 13g), which also created breaks in the stress–strain curve of bilayered films (Fig. 13h). PBAT/PHBV with PBAT serving as outer layer showed better resistance to water vapor 1.1–2.3 × 10^{-11} gm m^{-2} s^{-1} Pa^{-1} as well as tear resistance (7.4–11.6 N) in comparison with blends.[166]

Fossil-based hydrocarbons are cracked to produce olefins and further oxidized and derivatized to produce acrylates, which are then polymerized to produce polymers, resins, and coatings.[167] Alkoxybutenolides were chemically synthesized by using lignocellulose and converting it to furfural. Further applying photooxidation (using visible light) resulted in robust uniform thin-film coatings as a bio-based alternative for acrylate coatings for both glass and plastic materials.[167]

Compared with polysaccharides and proteins, melt and thermal processability of biopolyesters can be performed at higher temperatures, whereas this elevated temperature can cause polysaccharides and proteins to bear thermal irreversible deterioration. Laminates or coatings on biopolyesters are a reliable and emerging way for producing lightweight multilayer food packaging to minimize waste generation, reduce raw material use, and lower transportation costs.[81]

3.2.2.1 Polyhydroxyalkanoate (PHA) coatings. PHAs are biodegradable biopolyesters associated with "cradle-to-cradle" sustainability (*versus* "cradle-to-grave" dead end for oil-based resources)[168,169] and are considered the carbon source synthesized intracellularly by microorganisms.[168] The most commercially available types of PHAs are poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate) (PHBV) and poly(3-hydroxybutyrate) (PHB).[168] Thanks to PHAs' intrinsic hydrophobicity, they are good barriers against water vapor.[170] However, their mass production has been restricted due to the high price of raw materials, separation of PHA from biomass and low microbial productivity (3–4 g PHA per 1 h).[171,172]

Paper packaging is highly recommended with regards to the harmful effects of plastic packaging, since paper is derived from renewable cellulose fibers. However, paper suffers from having a low barrier against moisture, grease, and gas. Therefore, it is often coated or blended with petro-based materials to fulfill the packaging requirements;[7] however, this excludes such packaging from biodegradability or repulpability.[173] Therefore, investment in the PHA-coated paper industry as well as using PHAs in biocomposite materials can help to widen PHA applications and reduce their costs.

Several biopolymers have been coated on paper to improve the barrier properties. However, biopolymers suffer from a low oxygen and water vapor barrier.[174,175] To address this issue, three main strategies are often used: (1) development of nanocomposites, (2) functionalization of the biodegradable polymer, (3) coating paper with high barrier biodegradable polymers to develop multilayers.[176] Multilayers typically contain two layers called "barrier" (protects food against gas/water vapor) and "structural" (protects food against mechanical stress) on the inside and outside, respectively.[177] Another layer that can be included is the "active" layer.[162] In addition, adhesives or "tie" layer[177] resins are used to improve layers' adhesion (Fig. 14). The manufacturing of such multilayer systems is essential, in which every layer targets a specific property in the final paper packaging.

Coating methods include melt-extrusion, solution coating, dispersion coating and lamination,[173,178] of which extrusion coating is the most industrially established one. The preponderance of extrusion coating is due to (1) continuous processing, (2) forming uniform coatings, (3) negligible pinholes/cracks, (4) solvent-free application.[178]

A biocomposite solution based on PHB incorporating additives (*i.e.*, plasticizers, renewable fillers (potato starch or thermocell) and compatibilizer (stearic acid)) was coated on the paper by a film applicator.[181] The permeability of water vapor is higher in papers coated with PHB containing starch than those without starch due to starch's hydrophilic property and the heterogeneous structure of the biocomposite.[181] PHB/V was coated on the paper by extrusion-coating.[182] Regardless of the typically used pre-treatments (corona and flame) in extrusion coating, PHB/V coated papers showed sufficient adhesion only when the substrate's surface was pretreated with an acrylic primer. However, given that these primers are not biodegradable, their applications will be restricted where compostability is required.[182] In the second part of the previous study, WVTR and heat sealing of PHB/V coated paper were investigated. A higher crystalline melting point for PHB/V (50 °C) compared with LDPE (40 °C) resulted in the high sealing temperature for PHB/V coatings on paper. PHB/V coatings demonstrated four to six times poorer WVTR than that of LDPE coatings. However, the addition of tall-oil rosin or wax substantially improved the water vapor barrier properties.[183]

Using solvent casting to coat PHB on paper resulted in PHB infiltration into the cellulose pores, thereby reducing the paper's affinity to water molecules.[184] Similarly, biodegradable bilayers were prepared by coating PHB on cardboard *via* compression molding.[185] Films containing 15% of PHB showed a marked drop in water permeation, moisture content, as well as

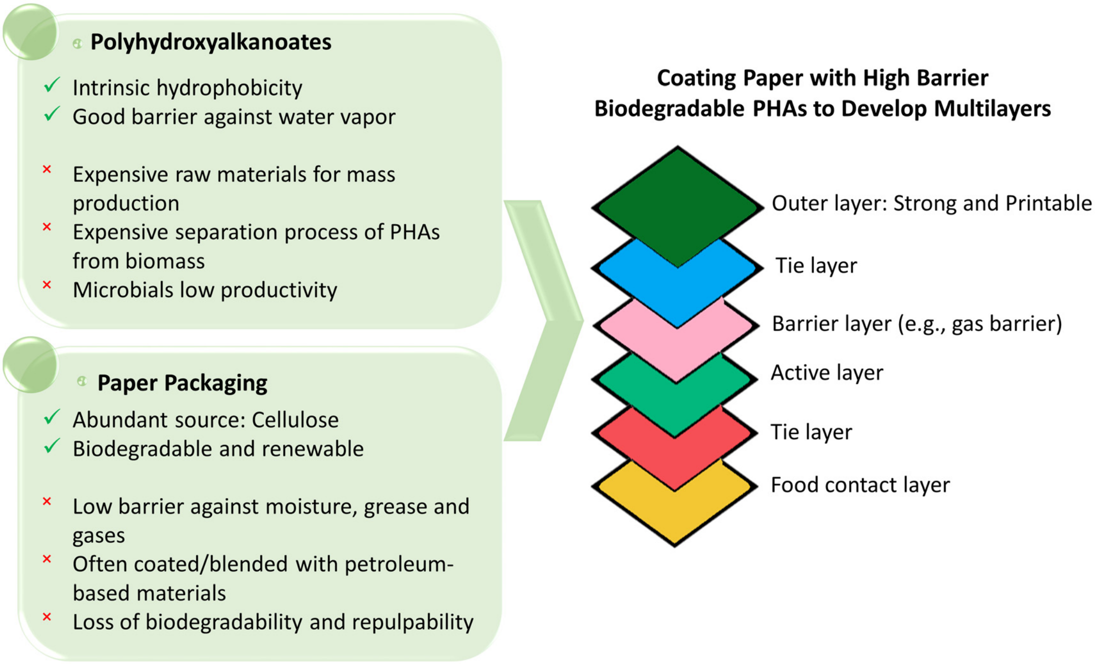

Fig. 14 Multilayered food packaging include printing layer, tie-layer, barrier layer, active layer and the food contact layer. The content of the figure on the right for multilayers is from ref. 179 and 180 and the figure is redrawn from ref. 180 with kind permission from John Wiley and Sons, copyright 2021.

polarity. Moreover, the cellulose cardboard was functionalized with acetic acid, resulting in lower moisture absorption than those without treatment.[185] Superhydrophobic papers were prepared by immersing papers in PHB-$CHCl_3$ solution and then in a coagulation bath consisting of water and ethanol.[186] To control the water flow through more wettable regions on the paper, argon treatment was used (Fig. 15a). Paper-coated PHB demonstrated higher WCA (*i.e.*, 153.0°) compared with original paper (110.4°), which stemmed from PHB hydrophobicity.[186] Exfoliated layered nanocomposite (PHBV-nanoclay) was coated on pre-sprayed paper with a PHBV suspension to enhance the resistance against water vapor.[187] The WVTR of the coated paper decreased to as low as 26.4 g m^{-2} day^{-1} at 90% relative humidity (RH) and 38 °C.[187]

A PHA latex emulsion was coated onto kraft paper and then the coated papers were treated with a rapid pulse of photonic energy.[188] This treatment resulted in molten PHA particles forming a continuous film within milliseconds without degrading the substrate (Fig. 15b). WVTR was approximately the same for both photonic-dried and conventional oven-dried samples. However, 2-min Cobb values were higher for photonic-dried coated papers, which was due to pinholes in the coated film.[188] The paper coated with triethyl citrate (TEC)-plasticized PHBV tore without releasing the coating from the paper at a bond strength of >1 N/15 mm, which shows the sufficient bond strength between layers (Fig. 15c and d)[189] compared with polyethylene glycol (PEG)-plasticized PHBV-coated paper.

Overall, the paper coating industry, which has high-volume production, is an appropriate field for utilizing PHA polymers without concerns about their high production costs.[181]

3.2.2.2 Polylactide (PLA) and PLA blends coatings. For every researcher in the field of biopolymers, polylactide (PLA) has been considered as a favorable biodegradable polyester as its polyester linkages come from 100% renewable resources.[190] This makes PLA one of the most viable replacements for petroleum-based polymers in the paper packaging industry.[191] However, a significant demand still exists for profitable routes to improve PLA barrier properties, thermal stability and reduce its brittleness.[176] Methods to tailor the PLA gas barrier include: (1) dispersing an additional phase(s) (*e.g.*, biopolymer, inorganic materials, nanofiller, fiber) into PLA continuous matrix to produce bio/nano composite blends; (2) modifying the PLA surface through hot pressing, wet casting, electrospinning, and co-extrusion. The first approach results in an intermediate barrier of the whole structure due to difficulty in dispersion and phase compatibility. However, the second approach results in a continuous blocking layer (or

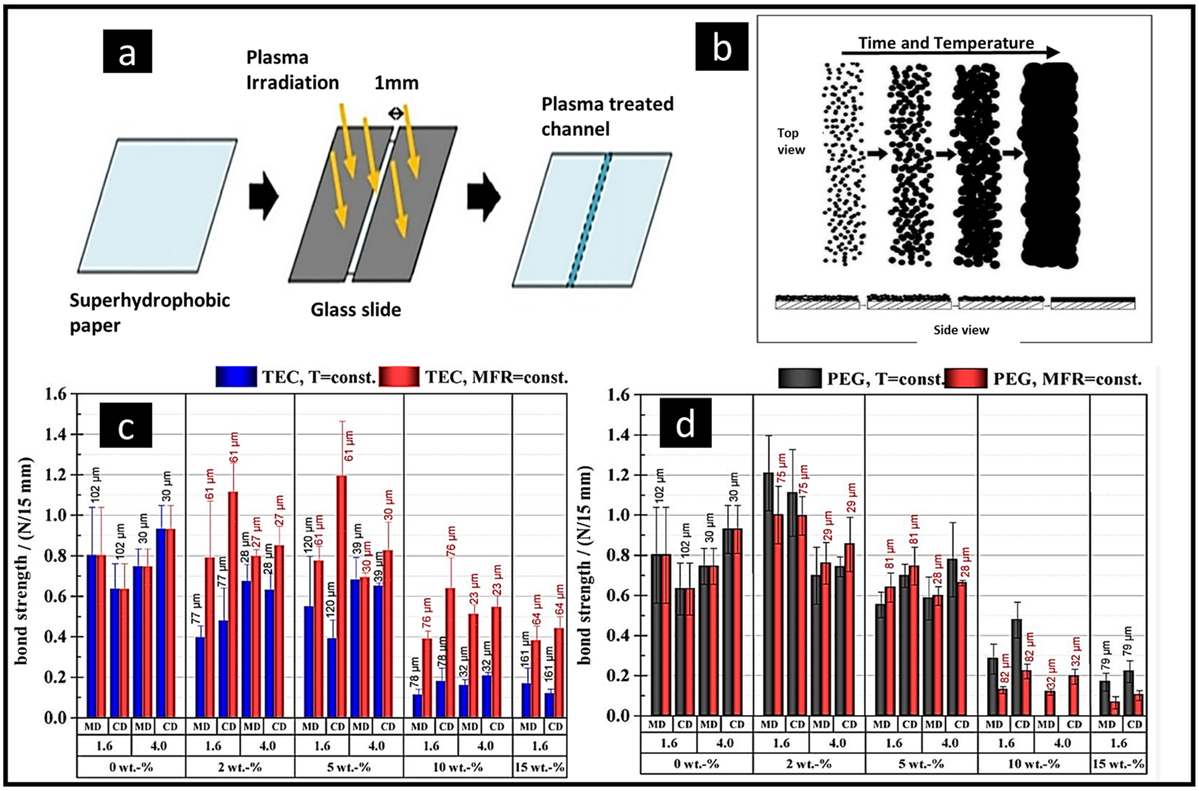

Fig. 15 (a) A scheme representing the type of processed patterning on the superhydrophobic paper. The exposed area to argon plasma is limited by glass slides, reproduced from ref. 186 with kind permission from Elsevier, copyright 2013. (b) Photonic energy heat treatment of PHA latex coated paper resulted in coalescing and interdiffusion of PHA particles to make a continuous film, Reproduced from ref. 188 with kind permission from TAPPI copyright 2018. (c) Bond strength of TEC-plasticized PHBV-coated paper and (d) PEG-plasticized PHBV coated paper, reproduced from ref. 189 with kind permission from MDPI copyright 2019.

laminate) on the surface to act as a barrier against permeant molecules.[42,192]

PLA solution was coated on paperboard for corrugated box liner applications. 3 w/v% of PLA solution resulted in the highest water barrier property. Multilayer tensile strength decreased compared with paperboard, while elongation at break slightly increased.[193] Thin multilayers were produced by coating a solution of cationic starch on baseboard to enhance the adhesion with the next layer, which was nanocellulose.[194] Next, PLA was extrusion-coated on the paperboard. Nanocellulose provides excellent oxygen resistance but a limited water vapor barrier, while PLA has high water vapor and low oxygen barrier.[194,195] The WVTR value of the multilayer was lower than WVTR of PLA and the reference (LDPE) coated baseboard.[194] The schematic of the coating process is shown in Fig. 16. The WVTR of the nanocellulose fiber-PLA nanocomposite (NCF-PLA)-coated paper depended on coating weight, temperature, and relative humidity.[196] Applying 1% modified NCF and higher coating weight resulted in lower WVTR values (34 g (m^2 24 h$)^{-1}$) compared with non-coated paper (1315 g (m^2 24 h$)^{-1}$).[196]

Low thermal instability of PLA is one of the major downsides of its usage in coating applications. To overcome this issue, the reinforcement of PLA with fillers (*e.g.*, nanoscale silicate) is needed.[197] Also, it reduces the manufacturing costs of the composite, enabling it to compete with low-cost polymers.[197] Hectorite, saponite, sepiolite[198] and montmorillonite[197] are some of the mainly used nanoclays incorporated

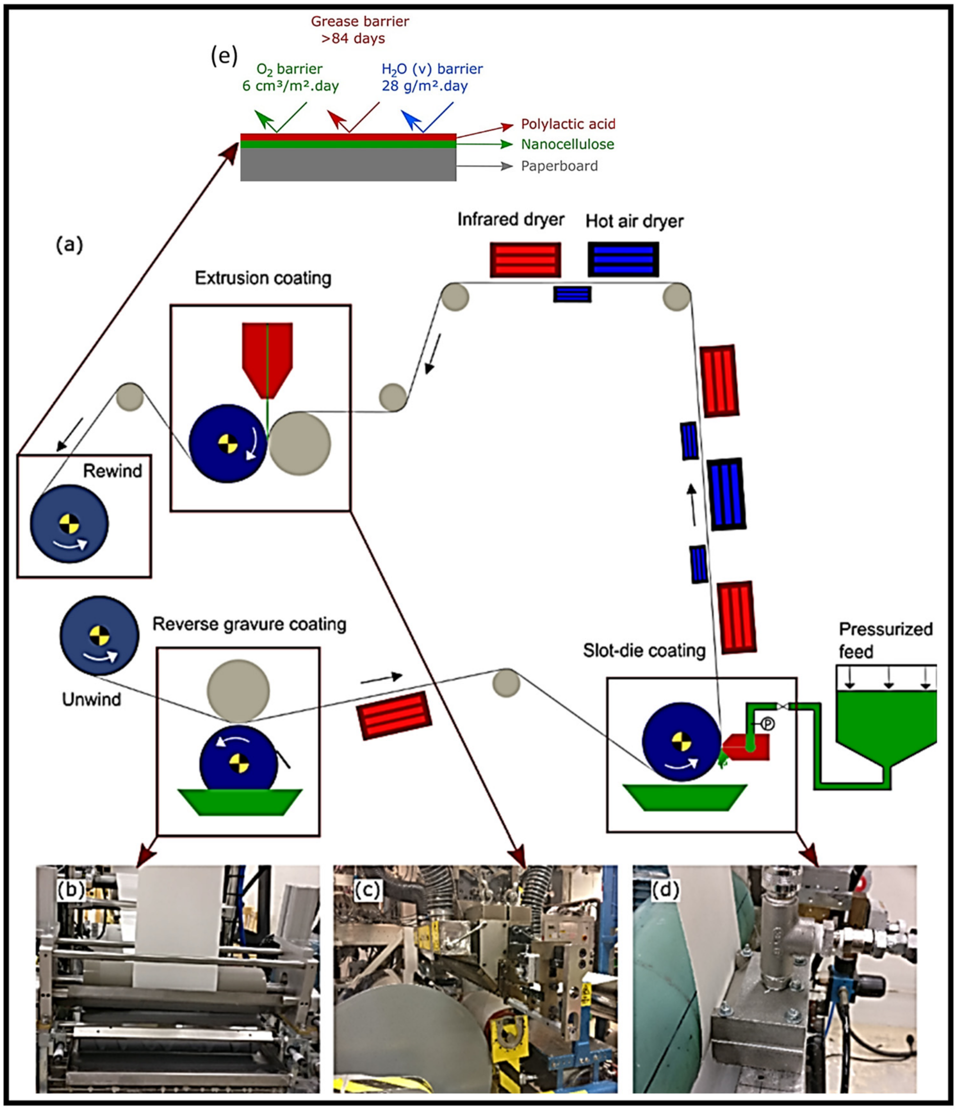

Fig. 16 (a) Illustration of the whole continuous line for coating of nanocellulose and PLA on baseboard, (b) cationic starch coating with reverse gravure method; (c) extrusion coating of PLA or LDPE (as the control); (d) nanocellulose coating with a slot-die; and (e) final structure of the coated paperboard, reproduced from ref. 194 with kind permission from ACS, copyright 2019 (open access) (https://pubs.acs.org/doi/10.1021/acsami.9b00922, further permissions related to the material excerpted should be directed to the ACS).

into PLA. Cheng *et al.*[199] modified PLA with gelatin to improve the adhesion as well as facilitate the lamination process of PLA on the paper substrate through enhancing the melt flow rheology of the polymer. Thin PLA-coated coffee cups could tolerate hot coffee or tea without any sign of leakage. The adhesion improved for PLA containing gelatin and the plastic coating played the role of a water barrier (WCA of 70.89°).[199]

So far, few researchers have paid attention to the "lotus leaf effect", imitating this through surface roughness modification to enhance water resistance/repellence properties in packaging materials. PLA electrospraying at 0.125% (w/v) over a pre-coated paper surface with 0.05 μm $CaCO_3$ starch-based coating significantly increased the water contact angle (151.29°) and improved WVTR, resulting in a superhydrophobic surface through forming a surface roughness hierarchical structure.[200] The PLA-PEG blend was coated on the kraft paper, using ethyl acetate to dissolve PLA instead of using hazardous halogen-based solvents (chloroform/dichloromethane). The total crystallinity was increased due to PEG addition, which improved gas barrier properties compared with neat PLA. Furthermore, the barrier properties against water, oil-grease, and water vapor as well as heat sealing properties of coated paper improved.[190]

3.3 Modifications of coatings

Coating technology is an emerging method towards the modification of surfaces to break limitations or meet challenges, particularly in food packaging applications. The modification process can be simply applying one coating layer on top of the surface or manipulating the formulation of the coating material to improve its properties and then applying it on the surface. Coating modifications are adopted to improve one or more properties, some of which are summarized in this section.

3.3.1 Environment resistance and barrier properties. The resistance of the packaging material against surrounding environmental factors such as water, oil, grease, UV, O_2 and CO_2 affects the final shelf life of packed food. Improving the barrier properties of the packaging material against these environmental factors is of high interest for improving food shelf life, thereby reducing food waste. Coating technology is commonly used in this regard to modify the surface properties of the base substrate (*e.g.*, paper, plastic) used for packaging, as discussed earlier in sections 3.1 and 3.2.

In paper coating applications, the modification of the coating with hydrophobic materials is performed to add water/oil repellency to the paper. For example, paper-coated chitosan-graft-castor oil improved paper hydrophobicity, originating from castor oil and surface roughness due to the presence of microspheres. Therefore, chitosan coating modification through grafting with castor oil improved the water/oil repellency of chitosan-graft-castor oil coated paper compared with chitosan-coated paper.[201] Surface coating modification of paper packaging, derived from oil palm fiber, with a beeswax–chitosan solution resulted in longer water absorbency time compared with uncoated paper.[202] Biodegradable water-resistant paper was made by coating ethyl cellulose on paper made from banana plants or water hyacinths. Banana plants and water hyacinths were chopped, ground, cast and dried separately to make papers.[203] To modify the paper against grease penetration, the fluoro-free grease proof paper was prepared by a non-toxic fluoro-free coating of sodium alginate (SA)/propylene glycol alginate and (SA)/sodium carboxymethyl cellulose. The coating resulted in a kit-value of maximum 9, showing potential applications for paper packaging that requires direct exposure to grease.[204]

Edible coatings are widely used in academia to improve the shelf life/safety of perishable fruits and vegetables, which tend to see biochemical and physiological post-harvest losses in a short time during transportation or storage. This issue results in economic loss and food wastage.[205,206] For instance, a lignocellulosic nanofiber/wheat gluten hybrid composite solution was dip-coated on six fruits (banana, cherry, grape, persimmon, waxberry, and litchi). The coated fruits showed resistance against microbes and UV as well as oxygen and water vapor permeation in comparison with bare fruits.[205] Dip-coating of perishable fruits (orange, mango, waxberry, strawberry and cherry) with biomimetic hybrid material derived from shellac membrane incorporating chitosan/poly(L-lactic acid) PLLA microspheres could improve the fruits' shelf life. The coating controlled gas (O_2, CO_2, H_2O) permeability and CO_2/O_2 selectivity. Further deposition of tannic acid on the microspheres imparted antioxidant and antibacterial properties to this hybrid coating material.[207]

Beeswax emulsion coating on tomato waste recycled cutin–pectin membrane produced a superhydrophobic artificial lotus leaf with an improved oxygen barrier. Further heating of coated membranes at 55 °C improved the adhesion of the layers as well as the water vapor blocking ability. The heated artificial lotus leaf showed anti-fouling ability against various food liquids such as milk, tea, honey, coke, energy drinks and yoghurt.[208] Bovine albumin–chitosan oligosaccharide was coated on a PLA biodegradable bag for strawberry preservation. The significant antibacterial properties of this coating postponed the decay of strawberries and maintained their freshness and brightness.[209]

PLA and cellulose possess the highest potential for commercialization in food packaging among other biopolymers, thanks to their abundant renewable natural resources. However, their commercialization is limited due to their high transparency to UV radiation. Surface modification of PLA and cellulose substrates by coating with *p*-coumaric acid and quinine improved their UV shielding property.[210] Similarly, the coating of carbon-dot-based solution on PLA and cellulose substrate greatly increased the UV barrier for usage in food packaging applications.[211]

Overall, surface modification of paper, plastic or films as well as foodstuff through coating technology or modification of coating formulation and subsequent application on the surface could effectively improve the surface functionality in terms of resistance against environmental factors such as O_2, H_2O, CO_2, UV, oil and grease. A summary of the recent literature is presented in Table 5.

Table 5 Application of coatings for improving the biodegradable polymeric substrate and food stuff against environmental factors

Substrate	Coating	Environment resistance	Ref.
Paper	Chitosan-graft-castor oil	• Improved hydrophobicity • Improved water/oil repellency	201
Paper from oil palm fiber	Beeswax–chitosan solution	• Longer water absorbency time	202
Paper from banana plant or water hyacinth	Ethyl cellulose	• Improved water resistance	203
Paper	Sodium alginate/propylene glycol alginate and sodium alginate/sodium carboxymethyl cellulose	• Improved grease resistance	204
Banana, cherry, grape, persimmon, waxberry, litchi	Lignocellulosic nanofiber/wheat gluten hybrid composite solution	• Resistance against microbes • UV shielding • Resistance against oxygen and water vapor	205
Orange, mango, waxberry, strawberry and cherry	Shellac membrane incorporated with chitosan/poly(L-lactic acid) microspheres and tennic acid	• Controlled gas permeability (O_2, CO_2, H_2O) and O_2/CO_2 selectivity • Antioxidant and antibacterial	207
Tomato waste recycled cutin–pectin membrane	Beeswax emulsion	• Superhydrophobic artificial lotus leaf • Improved oxygen barrier	208
PLA packaging for strawberry	Bovine albumin chitosan oligosaccharide	• Antibacterial • Maintained freshness/brightness of strawberries • Reduced spoilage of strawberries during storage	209
PLA and cellulose	*p*-Coumaric acid and quinine	• Improved UV shielding	210
PLA and cellulose	Carbon-dot-based solution	• Improved UV shielding	211

3.3.2 Coating performance – adhesion and heat sealability

3.3.2.1 Adhesion and coating delamination problem. To improve adhesion between coating and the substrate, characterizing the physio-chemical adhesion energy and coating/substrate interfacial tension is the key, and should be considered simultaneously to improve the final adhesion between coating and substrate. In forming a bond between coating and substrate, the researcher sacrifices both the coating surface (liquid) and the substrate surface (solid) and develops an interface. The adhesion energy measures how energetically advantageous the formation of an interface is. Interfacial tension refers to the inherent incompatibility that remains after the formation of the interface between coating and substrate.[90] The major factors that affect the adhesion can be divided into two groups: physical and chemical factors (Fig. 17). In addition, surface roughness, substrate wettability, and substrate preparation should be considered,[212] which are summarized below.

- *Substrate preparation*: Sufficient coating penetration into the substrate is necessary to make intermolecular forces. In this regard, the pre-treatment of the substrate with corona discharge or chemical modifications is useful to remove any oil, dirt, moisture, *etc.*[212] For instance, PLA coating on biaxially

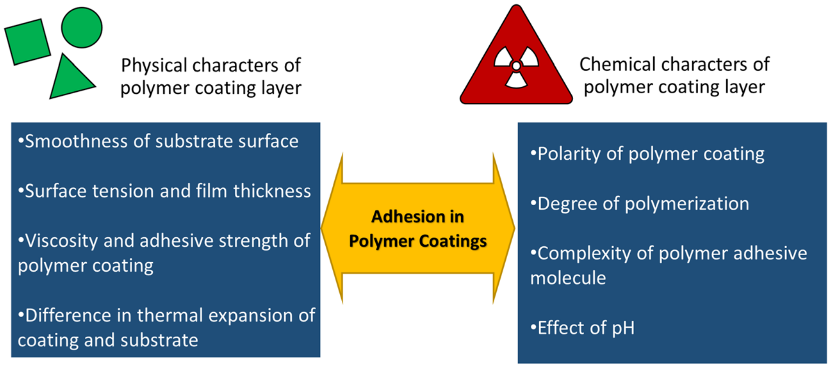

Fig. 17 Chemical and physical factors that affect the adhesion mechanism in polymer coatings. Physical factors include the smoothness of substrate surface, surface tension, thickness, viscosity, and bond strength of coating to the substrate. In addition, the variance in thermal expansion of coating and substrate affects the adhesion and a high difference results in weak bond strength during temperature variations. Chemical characters include polarity of polymer coating, degree of polymerization, complexity of polymer adhesive molecule (chain length and molecular weight of polymer coating) and pH. The figure is redrawn from ref. 212. Copyright (2020). From (Adhesion of Polymer Coatings) by (S. Verma and S. K. Nayak, S. Mohanty/Sanjay Mavinkere Rangappa, Jyotishkumar Parameswaranpillai, Suchart Siengchin). Reproduced by permission of Taylor and Francis Group, LLC, a division of Informa plc.

oriented PET (BOPET) was developed as a biodegradable sealant layer to improve the sealability of the substrate. The adhesion of the biodegradable PLA coating on BOPET was enhanced through corona treatment, resulting in the oxidation process and the presence of more polar groups.[213] In another effort for substrate preparation, to improve interlayer adhesion between molded pulp (MP) food trays and cellulose nanofiber/carboxymethyl cellulose (CNF/CMC), the MP was chemically modified by coating with chitosan solution. Chitosan provided electrostatic attraction with CNF/CMC, thereby improving the interlayer adhesion between CNF/CMC and MP.[214]

- *Surface roughness*: This is to create a rigid substrate, with peaks and valleys, to enhance the mechanical interlocking of the coating with the substrate.[212] For example, modification of acrylated epoxidized linseed oil with beeswax provided a stable wax–oil emulsion coating for paper packaging. Beeswax imparted microscale roughness on the surface of the coated papers, which resulted in improved hydrophobicity, thereby reducing WVTR.[215] Surface modification of paperboard with mineral-starch-based solution coating followed by electrospraying of an additional PLA layer imparted microscale roughness. Moreover, PLA particle agglomeration during electrospraying provided nanoscale roughness on the surface.[200]
- *Wettability and spreadability*: Complete wettability is achieved when the grooves and roughness of the substrate are filled with polymer coating rather than air. The air trapping causes a weak boundary layer on the substrate, which weakens the final adhesion. In addition, the polymer coating should be able to flow and spread at the micro/nanoscale onto the substrate to prevent the formation of gas pockets.[212] The synergy of coating rheology, film formation after the coating application process and substrate properties are required to achieve a smooth and integrated coating layer with sufficient flowability.[216,217] For example, adding glycerol as a plasticizer to chitosan/carboxymethyl cellulose softened the rigid crosslinked polymer network and showed shear thinning behaviour, thereby a good coating coverage and homogeneity were achieved on the paperboard substrate.[216]
- *Stresses*: The applied stress on a coated substrate transfers from the coating layer to the substrate or from one coating to another layer of coating in multilayers. This can be studied by fracture mechanics, which covers crack propagation along the coating–substrate interface, delamination, and failure.[212] For example, surface modification of paper by coating a low molecular weight chitosan solution of 0.25 wt% increased the tensile strength and modulus. In fact, chitosan filled the paper pores due to the strong interaction of chitosan and paper, increasing the stress-transfer from one fiber to another.[218] Environmental stress including atmospheric conditions and weather changes can also impact the coating performance negatively.[212] For instance, CNC coatings on PET surface showed a significant reduction in CO_2 barrier with increasing humidity from 0–80%, in which at 50% RH the CO_2 permeance value was close to uncoated PET. The same phenomenon occurred for the O_2 barrier of CNC-coated PET samples for RH >80%.[219]

3.3.2.2 Heat sealability. Flexible packaging needs to be securely sealed to avoid leakage of food content and to maintain the freshness of food. Various factors are involved in the sealing process, which are classified in four groups: processing factors, material characteristics, possible contaminant, and other required processes (Fig. 18). These factors are described in detail by Ilhan *et al.*;[220] however, the material characteristics in Fig. 18 are briefly discussed below in order to bring insight to researchers working on the development of coating materials.

- The **molecular weight (MW)** of the polymer used in flexible packaging affects the sealing process. There is an indirect relationship between molecular weight and diffusion through chain travel.[220] As MW increased, stronger seals and better interfacial adhesion were achieved. Also, a more homogeneous structure is provided by a narrow molecular weight distribution.[221] For example, in corn starch/chitosan film formulations, chitosan with medium molecular weight was selected to achieve better film-forming and heat-sealing properties rather than formulations with low molecular weight chitosan.[222] However, the effect of low molecular weight chitosan in these formulations has not been discussed.
- The **viscosity** of a molten sealant layer reduces with a rise in temperature. If the sealant layer becomes too liquid, it squeezes out from the seal area by excessive pressure. Nevertheless, by adjusting the process temperature in accordance with the properties of the polymer, the rheology of the melt polymer during the sealing can be controlled.[223] To prevent overheating and squeezing out, it is crucial to characterize the melt viscosity or melt flow index of the sealant for the specific process circumstances.[220,224] For example, celery paper was modified by soy-protein spray-coating to produce soy protein-celery composite paper with good heat-sealing properties. The shear thinning and viscoelastic behaviour of soy protein dispersion was the key to improving the heat-sealing properties of the coated celery paper. By increasing the soy protein concentration, its viscosity and seal strength increased.[225]
- The **amorphous fraction** of a melt polymer is correlated with the seal strength of the polymer at a specific sealing temperature because the non-melted crystal macromolecules establish a barrier to chain diffusion.[226] Therefore, the heat sealability of a highly crystalline polymer, such as PHBV, is difficult and tailoring its properties by blending or nanoparticle incorporation is necessary. Sealing in semi-crystalline polymers takes place around the crystal melt temperature,[227] since macromolecule mobility rises at the melting point. For example, the heat-seal initiation temperature for PBAT was decreased by either quenching (heat treatment) of PBAT or blending PBAT with PLA. In both ways, the crystallinity of PBAT decreased, resulting in higher chain mobility and diffusion, thereby higher adhesion strength at lower temperatures was achieved.[228]
- **Surface characteristic** of plastic coatings/films involves surface roughness and surface free energy. The wetting step of heat-sealing directly depends on the surface free energy of the material. The ability of plastic to adhere to other plastic increases, while having higher surface energy.[220] Corona discharge has been used as a surface treatment to increase surface free energy of materials as well as their wetting properties. On the other hand, surface treatment can give rise to

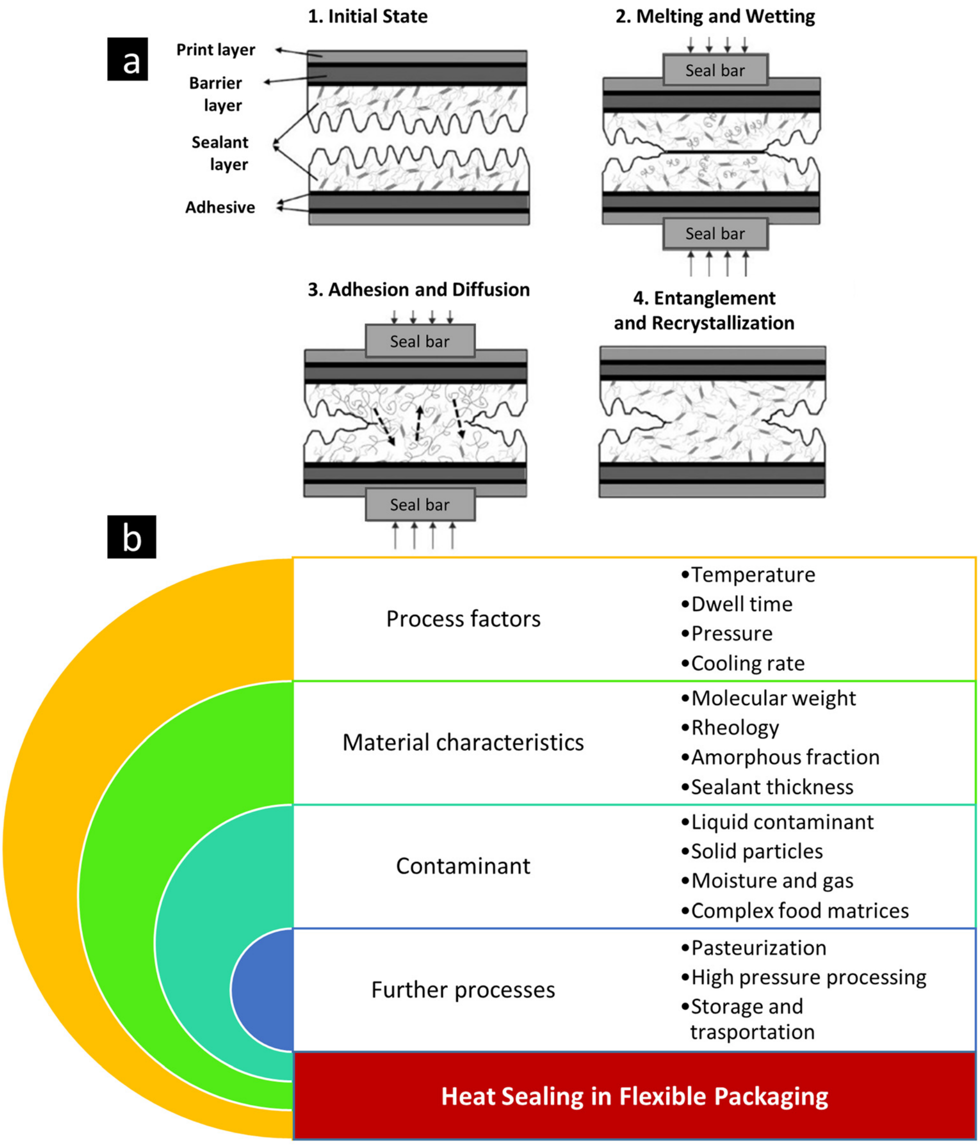

Fig. 18 (a) Heat-sealing mechanism in flexible food packaging.[220] (1 and 2) When two surfaces are melted and heated pressed, they make good contact (wetting) over the seal area. (3) Then, the chain diffuses across the interface, leading to molecular entanglements. (4) Segments undergo recrystallization after sealing, which binds the surfaces together and strengthens the seal. (b) Factors affecting final seal strength and seal integrity in flexible packaging. Figure (a) is reproduced and (b) is redrawn from ref. 220 by the authors with some modifications, with kind permission from John Wiley and Sons, copyright 2021.

surface roughness and results in improved wettability and adhesion.[220] Some examples of improving surface roughness are discussed in section 3.3.2.1.

- **Sealant layer thickness** also has a major impact on heat seal strength in barrier films because heat seal strength constantly rises with increasing sealant layer thickness above the seal initiation temperature.[229] However, greater squeeze-out issues are brought on by greater sealant thickness.[223] Contaminated particles, joints, and corners must be considered as the most crucial sealing sites in packaging, which need to be filled with enough sealant thickness.[220] For example, the seal strength and seal efficiency of bilayer fish gelatin/PLA films increased by increasing the ratio of fish gelatin layer thickness in fish gelatin/PLA bilayers.[230]

4. Challenges for biodegradable coatings

4.1 Processing and application of green coatings on food or food packaging

Polymeric coatings can be applied either on the food surface or on the desired substrate, which will be further used in food packaging applications. In both cases, the coating can have direct or indirect contact with the food and the FDA (Food and Drug Administration) information should be provided by the supplier of the food contact material. In addition, the functional barrier layer/component is responsible for the effective use of the coating. An appropriate efficient barrier blocks the migration of coating material to the food.[7] For example, techniques for assessing the migration of Ag and Cu nanoparticles (NP) from the coating and films to the food matrix have been reviewed by Ahari *et al.*[231] By using the titration method and the application of tetrazole with concentrated sulfuric acid, the migration of AgNPs from a polyamide film coated with Ag into caviar samples was investigated. No silver residual was found from packages with different AgNPs concentrations.[232] If the coating material has not migrated to the food, it is not considered a part of the food and therefore no regulations are applied to it. If there is no barrier layer/component between the food and the coating, the substrate must be revised for use with food under the desired application conditions. In the case of a migration study, to ensure that the testing is sufficient to support a safety determination, migration studies should be carried out in accordance with the FDA's chemical and toxicological guidance documents.[7]

4.2 Food safety consideration in coating technology (migration issue)

Various compounds found in food contact materials have the potential to migrate into the food and harm human health. Migrating substances can include non-intentionally added substances (NIAS) as well as intentionally added substances (IAS). In manufacturing coatings, IAS are known as commonly used ingredients, while NIAS are unknown materials found in the coating.[233] The toxicology information as well as *in vitro*/*in vivo* toxicology tests can be used to identify the IAS and NIAS hazards and determine the safety levels. NIAS can either be (1) wholly unidentified compounds, such as contaminants, degradation products, or other reaction products, or (2) anticipated chemicals based on chemical reactions involved in the production of food contact materials.[234]

Marin-Kuan *et al.*[234] reported that it is not viable to use the known time-consuming methods that entail the identification, quantification, and toxicological evaluation of all chemicals that have the potential to migrate to the food. An effort is being made to combine data from analytics, bioassays, and *in silico* toxicology techniques for the risk evaluation of packaging materials in accordance with the International Life Sciences Institute (ILSI) and the European Union (EU) recommendations on packaging materials.

It is important to note that there is a great debate about the application of edible coatings on foodstuff like fresh fruits and vegetables (FFV). Cloete *et al.*[235] highlighted that there is a wide disparity across different regions of the world on established regulations for edible coatings, and concluded that the industrial application of edible coatings are not fully viable.

Edible coatings with incorporated natural ingredients are considered as a solution to tackle the loss of highly perishable FFV by physical protection, reducing the pH losses, thereby extending shelf life.[235] In addition, consumer demand for safe, sustainable, and healthy food, has resulted in greater acceptance of natural edible coatings. On the other hand, a lack of standards and regulations, difficulties in scale-up, environmental sustainability concerns, and limited market research on consumer ideas and purchase intent, have limited the widespread application of edible coatings.[235] A recent survey on the consumer perception of FFV with edible coatings showed that 79.3% of the respondents would buy edible-coated FFV if it is approved by the FDA.[235,236]

For example, there are super hydrophobic edible coatings produced from FDA-approved (as generally recognized as safe (GRAS)) carnauba wax and beeswax for application on food containers to easily remove liquid food.[237] Xanthan gum-based coating on fresh cut lemon increased the storage time (at 4 °C) to 21 days.[238] In the US, most polysaccharides including xanthan gum that are used as major components in edible coatings are approved by the FDA.[235] Chitosan/tannic acid/corn starch bilayer films showed reduced WVP compared with chitosan film, and coating of these bilayer films on banana improved its storage time from 3 to 6 days.[239] However, tannic acid sensitivity to pH, light, and oxidation can cause a migration issue from the film.[240] Coatings and encapsulation of tannic acid have been reported to prevent its leaching and migration from the film to the food.[239,241] The edible coatings on fruits may cause disorders such as core flush, flesh breakdown, ethanol accretion and alcoholic off flavours, which are detrimental to fruit quality.[242,243] Transparent edible coatings have a preferable appearance for fruits and vegetables as customers can assess the food's external quality.[242] For example, whey protein-coated peanuts are reported to be darker than uncoated ones.[244]

Overall, edible coatings for FFV should be further explored in terms of their safety for human health, containing of allergic components, and consumer attitude as well as discovering cheaper coating materials and processes.

4.3 Processing of green coatings and their large scalability

The various coating methods have their own advantages and disadvantages and not all are suitable for large-scale coating production. Therefore, it is wise to select the coating method based on size and type of the substrate as well as surface roughness and final thickness of the thin film.[245] For example, spray or spin coating of a hydrophobic material at a large scale may result in a non-uniform surface.[37,246] Some of the advantages and disadvantages of different coating methods which have hindered their scale-up manufacturing are listed in Table 6.

To implement the laboratory-scale coating process in a large-scale application, it is also necessary to thoroughly solve the issues of safety material cost and long-term stability. It is

Table 6 Advantages and disadvantages of coating methods

Coating method	Advantage	Disadvantage or limitation in mass production
Spraying	• Minimal polymer use[245] • Any substrate size[245] • Requires low coat weights (around 10 g m^{-2}) to obtain the sufficient barrier properties (sometimes two layers are needed to remove the surface pinholes)[a] [178]	• Thicker layer ends up with uneven layer[245] • Liquid biopolymers and base substrates with chemical or physical sensitivity may be subject to limitations in liquid media[178] • Drying and solvent evaporation is energy-intensive[178]
Spinning	• Simple and rapid to create uniform coatings[245] • Thickness of a few nm(s) to a few microns after solvent evaporation[245] • Convenience and rather simple process setup[245]	• Difficult to control the coating thickness[178,247] • Sometimes need high amount of the solvent to prepare the coating solution • Solvent-based coating may cause any of below appearances to the final coating:[248] ○ Blistering ○ Bubbling ○ Sagging ○ Solvent lifting ○ Solvent popping
Dipping	• Quick, affordable, easy, and high-quality coating[178] • Applicable in both lab and industrial applications[245]	
Roll coating	• Most of the chemicals used in the roll-coating method are non-Newtonian fluids that behave in either a pseudoelastic or viscoelastic manner[245]	• Limited coating thickness range[249] • Time consuming clean up for change over from one coating to another[249] • Limited speed range[249]
Extrusion coating	• Continuous processing, minimal chances of pinholes and cracks, providing uniform coating[178] • Solvent-free application[178]	• Requires high coat weight to obtain the required properties[178] • Melt instability of the polymer[178] • Material-properties hinder the coating efficiency and coating speed[178]
Blade coating	• Good control over the coating thickness[178] • Adaptable for solvent free applications[245] • Large-area homogeneity[245] • Little material waste[245] • Interlayer dissolution prevention[245] • Quick-drying step prevents the traditional solvent annealing step[245]	• Can be confined up to pilot scale or laboratory[178]
Bar or rod coating	• Better control over the thickness of the coating layer[178] • The size of the groove or notch on the rod can be chosen to obtain desired coating thickness[250] • Relatively simple and cost effective[250] • Easy to clean the rod after coating[250] • Versatility in applying coating of different materials including liquid[250]	• Usually used on flat surfaces and may not work well on irregular surfaces[250] • Coating material viscosity and formulation affects performance of the coater instrument[250] • The operator skill and experience is critical to achieve an even and consistent coating (in case of coating manually)[250]
Other: physical/chemical vapor deposition (PVD and CVD), *etc.*	• Pinhole-free and uniform high barrier coatings and can provide chemical resistance and stress relaxation[35,251,252] • High deposition rate and low deposition temperature[47] • CVD is the most popular method to obtain highly uniform coatings on 3-D substrates[47] • CVD provide multidirectional deposition[253] • PVD provides full control over growth, pristine film quality, large-scale fabrication, co-deposition flexibility, and controlling of the deposition temperature[253]	• Toxic gas can possibly be released from the reaction[47] • Substrate temperature may cause phase changes or grain growth and diffusion of dopants in microelectronic components[47] • The corrosive gas can lead to poor adhesive between coated film and substrate and contaminate the film[47] • Pricey vacuum environment and expensive instrumentation[245] • PVD provide only linear type of deposition[253]

[a] Although this is true for generally solvent-based coatings methods, the thermoplastic polymer used in the coating can influence the required coating weight. For example PLA coating by extrusion or solvent coating requires high coating weight to obtain necessary barrier properties, while solvent or dispersion coating of other biopolymers need lower coat weight to get sufficient barrier properties.[178]

important to make sure that all components of the coating are safe. For example, many different kinds of nanoparticles are still generally dangerous to human health and pose a threat to public safety. Creative engineering approaches can be used to reduce the number of nanoparticles that leak into the environment. Further research and development can be performed to lower the loadings of relatively expensive nano additions or to find less expensive substitutes that can provide comparable qualities and performance to lower the cost of materials. The long-term chemical and physical stabilities of the materials should also be enhanced considering that these coating materials would likely be exposed to outside natural factors such as heat, rain, humidity, and UV radiation for a long period of time.[37]

The development of various functional coating materials with desirable qualities and performance, as well as enhanced adoptability for large-scale applications in our everyday life, is anticipated to speed up through ongoing research in the field of sustainable materials. However, scale-up requirements and corresponding costs, technical feasibility for commercial viability, and life-cycle assessment as well as practical biodegradability are yet to be studied, discussed, and implemented. Some of the steps for these issues are addressed below.

- Manufacturing the multilayer coatings out of biopolymers requires the appropriate materials and equipment, which are affordable and economically capable for mass production.
- After multilayer packaging is successfully manufactured on a large scale, its performance should be monitored during storage, distribution, and consumption by customers to systematically analyze its quality and deficiencies.
- It is also needed that government regulations develop in a way that educates people about the advantages of novel kinds of packaging materials in regards to the environment, since consumer acceptance of these materials is an important factor for their mass production.

4.4 Green chemistry and sustainability needs in polymeric coatings

Despite a substantial movement over the past few decades from solvent-based coatings to more ecologically friendly water-based coatings, solvent-based coatings are still widely used in some applications. While high-end flexible packaging, such as that used for coffee and tuna food containers, is predominantly solvent-based, low-end flexible packaging is now predominately water-based. Pressure-sensitive adhesives are primarily water-based, whereas industrial adhesives are predominately solvent-based. Flexible packaging materials are similar to coatings in that they are made of a number of thin polymeric layers and are intended to protect its contents from environmental exposure.[254] Some of the developed green principles and new ideas are summarized below.

- Utilization of biobased building blocks instead of petrochemical monomers. For example, a continuous, clear, and water-resistant coating was achieved from evaporation of CO_2 and water from the cast film of carbon dioxide switchable polymers. During evaporation, these polymers switch from hydrophilic to hydrophobic. Since these polymers are soluble in carbonated water rather than natural water, they may keep the VOC-free advantage of water-based coatings and are a substitute for solvent-based coatings.[255]
- Biosourced nanoparticles can operate as efficient Pickering stabilizers, providing potential alternatives to traditional surfactants.[256–258] Current research has demonstrated that bio-surfactants are efficient in emulsion polymerization.[259] Additionally, research is being done on innovative ways to add starch nanoparticles directly to emulsion polymers (latexes) to boost their bio-content.[260,261]
- Novel flame-retardant multilayer coating was developed by the incorporation of chitosan instead of bromine-based materials.[262]
- There have been reports on bio-based, biodegradable thermosets made from epoxidized sucrose soyate, which is produced by epoxidizing sucrose ester resins obtained from soybean oil fatty acids.[263,264] Utilizing carboxylic acid-containing moieties from naturally occurring sources, such as fruit juices, will result in crosslinking, producing an alternative to petroleum-based thermoset resin used in coatings.

Overall, using green chemistry principles, products that enable biodegradation or make recycling easier at the end of the product's service life would be beneficial, and have the potential to be industrially commercialized.

5. Conclusion and future works

In this review paper, we focused on the promising potential of biodegradable coatings to boost polymeric substrate properties to be used as a viable alternative for petroleum-based food packaging materials. The modification of biodegradable substrates, either paper or plastic, with a coating layer or modification of coating formulation are reviewed with the focus on the improved water vapour and oxygen barrier performance of the base substrate. In addition, the effect of coatings on the mechanical characteristics of the substrate or adding new functional properties to the substrate (*e.g.*, antimicrobial, antioxidant) are briefly discussed.

We have discussed various biodegradable coatings based on biopolymers from nature (*i.e.*, lipids, proteins, polysaccharides, biomass, and agriculture waste), as well as bacterial polymers (*i.e.*, PHAs) and synthetic/biobased biodegradable polyesters that are used to tackle the shortcomings of biodegradable substrates for food packaging applications.

Firstly, in terms of barrier properties, coatings represent a primary strategy for enhancing the barrier characteristics of biodegradable substrates. To protect food against moisture, hydrophobic materials are the most effective barrier coatings, such as lipid, waxes and PHAs. Proteins and polysaccharides have a poor moisture barrier due to their hydrophilic nature. However, proteins and polysaccharides possess better barrier against gases compared with lipids. Secondly, in regards to mechanical properties, protein-based coatings exhibit superior performance in comparison with coatings based on polysaccharides or lipids. In general, for coatings to improve the barrier and mechanical properties, bonding and interlocking with the substrate is necessary and any delamination failure can have a negative effect on the performance of the coated substrate. Lastly, coatings have the capacity to impart antimicrobial or antioxidant attributes to the underlying substrate. In this context, examples include lipids (*e.g.*, essential oils) and polysaccharides (*e.g.*, chitosan and pectin), as well as the modification of coatings through the integration of inorganic materials such as ZnO nanoparticles.

Overall, multilayer packaging, compared with single-layer packaging, has more capacity to boost the performance of biodegradable-based materials, particularly regarding barrier properties. It is noteworthy to stress that, to meet sustainability goals, many companies that manufacture consumer packaged goods have stated they will introduce new paper-based or other sustainable bio-based polymer packaging by 2025–2030.[34,265,266] Moreover, the challenges of biodegradable coatings such as adhesion and delamination of layers, heat sealability, and migration of coating material to the food, which hindered the mass production and application of coatings, are discussed, and possible ideas to tackle these challenges are provided. Finally, a few recommendations for future research are given separately below on the application of biodegradable coatings on paper and plastic packaging.

5.1 Biodegradable coatings on plastics substrates

- Nowadays, PLA is commonly used in many kinds of flexible bio-packaging. However, a coating or surface metallization is required to boost its gas-barrier properties.[81,267] After reviewing the literature, we suggest that an appropriate natural barrier coating would eliminate our reliance on petroleum-based or metallized coatings.
- Cellulose and its derivatives have been applied as nano coating or laminate layers with other biopolymers. However, there is room for exploring cellulose as a laminate layer with other biopolymers.[81]
- Lipid-based materials such as waxes that are intrinsically hydrophobic can be further explored as a coating layer on the biopolymers to improve their barrier against water vapor permeation.
- Another untapped area is the creation of structured nanoparticles from biopolymers such chitosan, alginate, and zein as barrier coatings.
- Coating or laminating biopolyesters on one another is another research area that needs to be explored more particularly to improve the barrier of the final multilayer against oxygen and water vapour.

5.2 Biodegradable coatings on paper substrates

- Effective coating of non-polar biopolymers such as PLA, PHB and PHBV on paper improves its water barrier properties. PHB in particular has shown the most comparable WVP to PE, which is currently used as a petroleum-based coating for paper packaging.[178,268]
- To further improve the barrier properties of hydrophilic biopolymers, one strategy is to make a blend of them with lipid-based biopolymers or hydrophobically modified biopolymers, or using these polymers as a filler.[268]
- Biopolymers from nature which are polar, such as cellulose, starch and protein, are easily permeated by water vapour, in particular at high humidity.[269,270] Hence, for their effective application as a coating on paper, their surface treatment to act more hydrophobically is essential.[268]
- Biopolymers that are highly crystalline, such as micro/nanofilbrillated cellulose (MFC, NFC), showed excellent barrier properties, even better than conventional polymers for paper substrates.[178]

In closing, it is worth emphasizing that polymeric coatings provide society with a variety of sustainability benefits by increasing product lifespans, lowering maintenance requirements, and/or defending our health and well-being. Due to the manufacturing process of bi- or multilayer laminates, they have the ability to conceal certain undesirable shortcomings of biodegradable substrates while showcasing their desired properties.[81] The development and research on coating technology is in progress to make lightweight packaging materials; however, our review suggests that we still have a long way to go in developing packaging materials which can prove to be a great competitor for conventional plastics in terms of cost effectiveness and consumer acceptability, besides being renewable, environmentally friendly and sustainable.

Abbreviations

VOC	Volatile organic compound
UV	Ultraviolet
PVdC	Polyvinylidene chloride
PVC	Polyvinyl chloride
PE	Polyethylene
PP	Polypropylene
LDPE	Low-density polyethylene
HDPE	High-density polyethylene
PS	Polystyrene
PET	Polyethylene terephthalate
PHAs	Polyhydroxyalkanoates
P3HB	Poly(3-hydroxybutyrate)
PHBV	Poly(3-hydroxybutyrate-*co*-3-hydroxy valerate)
PBAT	Poly(butylene adipate terephthalate)
PLA	Polylactic acid
WG	Wheat gluten
TPS	Thermoplastic starch
ASTM	American Society for Testing and Materials
ESBO	Epoxidized soybean oil
PBS	Polybutylene succinate
PCL	Polycaprolactone
PVOH (PVA)	Poly(vinyl alcohol)
PBSA	Poly(butylene succinate adipate)
IUPAC	International Union of Pure and Applied Chemistry
BW	Beeswax
CW	Carnauba wax
WPI	Whey protein isolate
WVP	Water vapour permeation

WVTR	Water vapour transmission rate
OP	Oxygen permeation
OTR	Oxygen transmission rate
RH	Relative humidity
LBL	Layer by layer
ALG	Alginate
PEI	Polyethylenimine
CGG	Cationic guar gum
TOCNs	TEMPO-mediated oxidized cellulose nanofibrils
TPCS	Thermoplastic corn starch
PWS	Plasticized wheat starch
CMC	Carboxy methyl cellulose
HPC	Hydroxy propyl cellulose
MC	Methyl cellulose
PBT	Poly(butylene terephthalate)
MTPS	Maleated thermoplastic starch
TPS	Thermoplastic starch
SEM	Scanning electron microscopy
AFM	Atomic force microscopy
MA-g	Maleic anhydride grafted
PdNP	Palladium nanoparticle
CNC	Cellulose nano crystal
OEO	Oregano essential oil
TEC	Triethyl citrate
PEG	Polyethylene glycol
WCA	Water contact angle
NCF	Nanocellulose fiber

Author contributions

F. J.: methodology, investigation, data curation, formal analysis, visualization, writing – original draft. A. K. M.: conceptualization, investigation, methodology, validation, supervision, resources, writing – review & editing. M. M.: conceptualization, investigation, methodology, validation, supervision, resources, funding acquisition and administration, writing – review & editing. All authors contributed to discussion, reviews, editing and approval of the manuscript for publication.

Conflicts of interest

The authors declare no conflict of interests.

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