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REVIEW ARTICLE

# Perspectives on Utilization of Edible Coatings and Nano-laminate Coatings for Extension of Postharvest Storage of Fruits and Vegetables

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**Abstract**  It is known that in developing countries, a large quantity of fruit and vegetable losses results at postharvest and processing stages due to poor or scarce storage technology and mishandling during harvest. The use of new and innovative technologies for reducing postharvest losses is a requirement that has not been fully covered. The use of edible coatings (mainly based on biopolymers) as a postharvest technique for agricultural commodities has offered biodegradable alternatives in order to solve problems (e.g., microbiological growth) during produce storage. However, biopolymer-based coatings can present some disadvantages such as: poor mechanical properties (e.g., lipids) or poor water vapor barrier properties (e.g., polysaccharides), thus requiring the development of new alternatives to solve these drawbacks. Recently, nanotechnology has emerged as a promising tool in the food processing industry, providing new insights about postharvest technologies on produce storage. Nanotechnological approaches can contribute through the design of functional packing materials with lower amounts of bioactive ingredients, better gas and mechanical properties and with reduced impact on the sensorial qualities of the fruits and vegetables. This work reviews some of the main factors involved in postharvest losses and new technologies for extension of postharvest storage of fruits and vegetables, focused on perspective uses of edible coatings and nano-laminate coatings.

## Introduction

Around the world, agriculture and food industry suffer significant product losses from harvest to consumer, due to different factors involved. Such losses depend firstly on the management conditions existing in each region as well as on its economic resources. Thus in industrialized countries, more than 40 % of the food losses (including cereals, roots and tubers, oilcrops and pulses, fruit and vegetables, meat, fish and dairy) occur at retail and consumer levels, while in developing countries, more than 40 % of the food losses occur at postharvest and processing levels [52]. In the year 2011, Latin America presented the highest percentages of postharvest handling and storage losses (PHSL) in crops (28 %), while in industrialized countries (Europe and North America and Oceania), the percentages of PHSL were considerably minor (18 and 16 %, respectively; Table 1) [52].

Moreover, the largest postharvest losses in fruit and vegetable crops are due to deterioration caused by microorganisms after harvest and during cold storage. Fruits, due to their low pH, higher moisture content and nutrient composition are very susceptible to the attack of fungi, while vegetables are generally less acidic, and their spoilage is usually by bacteria [60, 116]. Although it is very difficult to determine the full extent of postharvest losses due to decay (i.e., attack by microorganisms and physical damages), it is well-known that these losses are significant [78].

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**Table 1** Estimated/assumed postharvest handling and storage losses by region

| Crop group[a] | Postharvest handling and storage losses by region (%) | | |
| --- | --- | --- | --- |
| | Europe (incl. Russia) | North America and Oceania | Latin America |
| Cereals | 4 | 2 | 4 |
| Fruits and vegetables | 5 | 4 | 10 |
| Roots and tubers | 9 | 10 | 14 |

Adapted from Gustavsson et al. [52]

Fruits and vegetables: oranges and mandarins, lemons and limes, grapefruit, other citrus, bananas, plantains, apples, pineapples, dates, grapes, other fruit, tomatoes, onions, other vegetables

Roots and tubers: potatoes, sweet potatoes, cassava, yams, other roots

[a] Cereals (excluding beer): wheat, rice (milled), barley, maize, rye, oats, millet, sorghum, other cereals

The use of simple postharvest practices (e.g., selection of suitable harvest timing by maturity indices, cleaning of the product, sorting, packaging, quick cooling and good refrigerated storage and appropriate transportation and distribution) has been successful for small farmers when they are correctly applied. However, these practices do not always guarantee the produce integrity forcing producers to apply several treatments during postharvest preservation of food crops [126]. Chemical treatment is one of the postharvest techniques that are normally used before and after harvest to prolong shelf life and reduce food spoilage [36]. However, the lack of regulation in less developed countries has generated the indiscriminate use of pesticides in fruits and vegetables allowing the improvement of resistance of plagues to the most acceptable pesticides, while also affecting human health. Many of those pesticides have thus been removed from the market [17], consequently reducing the options for convenient and safe treatment of crops. Physical and quality losses are also due to deficient storage conditions, use of poor quality packages, rough handling, and a lack of suitable tools for postharvest management. These are the main reasons for losses of crops' market value and food safety, thus leading to low incomes for producers [66].

The increasing consumer demand for fresh fruits and vegetables of higher quality and more nutritious has encouraged the food industry to develop new and better methods for maintaining food quality and extending shelf life [9]. Recent studies of postharvest treatments, particularly the use of edible coatings and nano-laminate coatings, are receiving a growing interest by food industry. It is known that producers in developing countries are largely small farmers, rarely associated with formal organizations; therefore, the access to technical training, and in general, new postharvest technologies, is limited; also the scarcity of information about costs and financial benefits of using these new technologies is a problem. The implementation of a technology from the laboratory to the field represents an area of opportunity [65, 66].
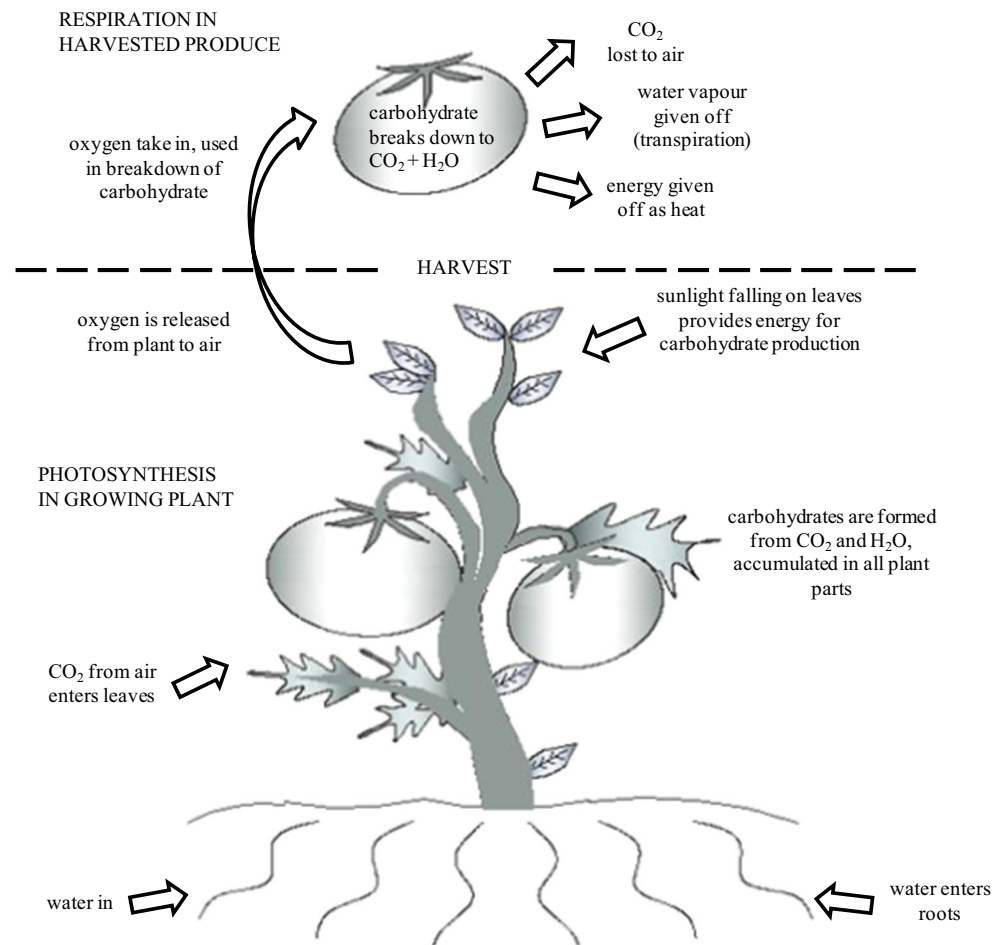
This review presents a new insight about the application of edible coatings and nano-laminate coatings as potential postharvest technologies for fruits and vegetables storage.

## Parameters Involved in Fruit and Vegetables Postharvest Losses

During harvesting, fruit and vegetables continue living despite being separated from their natural source of organic and mineral nutrients and water. The energy used to conduct these activities results from the respiration process; it involves the breakdown of carbohydrates to produce carbon dioxide, water and heat (Fig. 1). Also, the transpiration process takes place moving water vapor from the plant organs' surface to the surrounding air (Fig. 1) [26, 121]. These processes do not continue indefinitely, causing initial shrinkage and subsequent weight loss of the tissues (about 5–10 % of their weight) [42]. Both respiration and transpiration processes are considered as the major causes of postharvest losses and poor quality in produce, and their control is important in order to extend produce shelf life [11].

The control of relative humidity (RH) and temperature of storage is also important, since these are factors that play an important role in maintaining produce quality due to the direct influence they have on transpiration and respiration processes, as well as on the vapor gradient between the produce and the storage atmosphere. Then, when the produce is kept at a temperature similar to that of the storage environment, transpiration rate is highly correlated with the RH during storage [121]. It has been shown that high RH values during storage can reduce moisture losses and subsequently maintain fruit firmness by decreasing the transpiration rate of fruits or sub-cuticle evaporation, mainly under reduced air velocities and low temperature [56]. In addition, low temperature (4–8 °C) can reduce respiration rate, increase tissue resistance to ethylene action, delay compositional breakdown of macromolecules, retard senescence, and control the development of rot microorganisms [126]. However, at such temperatures, some tropical native fruits and vegetables can present chilling injuries. Due to the influence of these factors (i.e., RH, temperature), each produce has its own ideal set of conditions that allow a successful storing for the maximum length of time, although RH levels around of 85–95 % are commonly recommended for the storage of fresh fruits and vegetables [121].

**Fig. 1** Processes involved in the respiration of harvested produce

RESPIRATION IN HARVESTED PRODUCE

carbohydrate breaks down to $CO_2 + H_2O$

$CO_2$ lost to air

water vapour given off (transpiration)

energy given off as heat

oxygen take in, used in breakdown of carbohydrate

HARVEST

oxygen is released from plant to air

sunlight falling on leaves provides energy for carbohydrate production

PHOTOSYNTHESIS IN GROWING PLANT

carbohydrates are formed from $CO_2$ and $H_2O$, accumulated in all plant parts

$CO_2$ from air enters leaves

water in

water enters roots

On the other hand, decreases in yield and quality of fruits and vegetables caused by pest damages (especially by fungi) during storage can be even higher than losses occurring in the field, and these are favored when the produce is not rapidly cooled or is not transported and stored in appropriate conditions [10]. Commonly, chemical treatment is a postharvest technique used before and after harvest to prolong shelf life and reduce food spoilage [36].

The use of biopesticides has emerged as one alternative substitute for chemical pesticides. Biopesticides are certain types of pesticides manufactured from living microorganisms (e.g., bacteria, fungi or viruses) or plant extracts (including secondary metabolites and essential oils) and other biochemicals (e.g., insect sex pheromones) [6, 24]. The increasing use of this kind of biocontrol is demonstrated with the recent approval of more than 430 biopesticides active ingredients and 1320 active products on the list of Environmental Protection Agency (EPA) [35].

Within microbial-based biopesticides, the use of antagonistic microorganisms, mostly bacteria and fungi, has shown their efficiency to control different postharvest rot pathogens of sweet cherries and table grapes [105], banana [27], citrus [18], pineapple [124], apple [76, 110], peach [95], potato

[99], tomato [70], and mandarin [59], among others. However, this type of biopesticides presents some disadvantages according to tests conducted under commercial or semi-commercial conditions. More in detail, the use of formulated biopesticide preparations leads to inconsistency and variability in disease control level, being this one of the most significant barriers preventing widespread implementation of biocontrol technology [33, 36]. Indeed, simple application of antagonistic microorganisms does not provide comparable control results to chemical pesticides [34], although it has been proven that the combination of antagonistic agents with innocuous exogenous substances, such as chitosan, amino acids, antibiotics, calcium or bicarbonate salts, has increased the level of protection against *Penicillium digitatum* and *P. italicum* on oranges [84].

Another promising alternative to chemical pesticides is the use of biopesticides based on plant extracts and essential oils (EOs) of aromatic plants [67]. These are denominated green pesticides since they are obtained manly employing organic solvents (e.g., water, ethanol, methanol and hexane). It is known that the antimicrobial activity depends on plant species as well as on the nature of solvent extract used; in this order, several works have been focused in obtaining new

plant extracts and essential oils with acceptable antimicrobial activity [20]. Recently, methanolic extracts from nine wild edible herbaceous species showed the highest efficacy (in vitro and in vivo) against some important postharvest pathogens, i.e., *Botrytis cinerea*, *Monilinia laxa*, *P. digitatum*, *P. expansum*, *P. italicum*, *Aspergillus carbonarius*, and *A. niger*; the inhibition efficacy of these extracts was associated with the presence of some caffeic acid derivatives and/or flavonoids [49]. Moreover, Jasso de Rodríguez et al. [62] reported effective antifungal activity (in vitro) of hexanic and ethanolic extracts of Mexican semi-desert plants against *Rhizopus stolonifer*, *Colletotricum gloesporoides* and *P. digitatum*; the authors reported that the effectiveness depends on the nature of extracting solvent used.

Biopesticides are accepted worldwide; however, their utilization still faces some important challenges such as: (1) poor stability—this is the major drawback of these products, which need improvement of their formulations for a better market acceptance; (2) packaging—it should be designed in such a way that the stability of the packaged products can be maintained during storage (e.g., no container swelling due to the growth of spoilage microorganisms); (3) shelf life—biopesticides shelf life is often low; (4) highly specific activity—causing that biopesticides will be niche products (thus with significantly lower sales) when compared with chemical products, with a broad spectrum of activity; and (5) distribution—being the major obstacle due to higher cost, leading to lower margins and limited training for sellers, distributors and farmers [122].

An attractive alternative to overcome these disadvantages and generate new postharvest technologies can be the incorporation of active agents used in formulation of biopesticides into edible coatings. The use of edible coatings can increase biopesticides' stability and shelf life and at the same time add new functionalities to the final product (e.g., decrease packaging gas transfer rates).

At this moment there are only a few biopesticide-based products applicable in the postharvest stage, since most of them are aimed at controlling preharvest pests. Also, it is known that most of the biopesticide producing companies are medium and small enterprises, therefore having limited resources for R&D, product registration and promotion [24]; this highlights the importance of developing new and inexpensive technologies such as coating-based technologies.

## Edible Coatings to Increase Quality and Shelf Life of Fruit and Vegetables

Currently, edible coatings have been successfully introduced in food processing due to the beneficial impact on the produce quality and environment, since they preserve the organoleptic properties of foods, retard moisture loss, create a barrier for gas exchange between the fresh fruit and the surrounding atmosphere, and reduce the use of disposable and non-degradable packaging materials, maintaining their organoleptic properties [108, 120]. The major advantage of edible coatings is that they can be consumed with the packaged products [14]; therefore, all components used in their formulation should be classified and recognized GRAS (generally recognized as safe) and should have been approved to be consumed with the food products. Most edible coatings are based on polysaccharides, proteins and lipids, being used alone or in blends [72]; their mechanical and barrier properties depend strongly on the physical and chemical characteristics of their constituents [90].

### Lipids

Lipid-based coatings are commonly made from waxes (e.g., carnauba wax, beeswax and paraffin wax), oils (e.g., mineral and vegetable oil) and resins (e.g., shellac wood rosin, coumarone-indene resin) [72]. These coatings have low polarity and because of that are effective for reducing water transmission [115]. Moreover, they provide protection on chilling injury and improve the appearance of the produce [32]. These coatings have been extensively used on whole fruit and vegetables; however, they show some disadvantages such as formation of cracks, lack of homogeneity, sensorial alterations, poor adhesion to the produce, and in some cases, the high gas barrier they establish leads to anaerobic conditions [8, 28]. Their combination with polysaccharides or proteins may interact favorably, resulting in edible coatings with a good mechanical strength and controlled barrier characteristics [25, 119].

### Proteins

A variety of proteins from natural sources have been used for edible coatings production, some examples are: casein, whey protein, collagen, gelatin, keratin, wheat gluten, soy protein, peanut protein, corn-zein and cotton seed protein [31]. These coatings usually exhibit good mechanical properties since they are structured by 20 different monomers (amino acids), allowing high potential for forming numerous linkages via disulfide (S–S) covalent bonding, electrostatic forces, hydrogen bonding and hydrophobic interactions. Protein-based coatings also present good oxygen barrier properties at low RH, although most of them are poor barriers against water vapor due to their hydrophilic nature [15]. Several procedures, including chemical and enzymatic modification of protein properties, combination with hydrophobic materials, and physical methods, have been performed in order to improve their barrier and mechanical properties [15].

## Polysaccharides

Polysaccharide-based coatings have been the most commonly used to coat fruits and vegetables due to their appropriate adhesion and flexibility properties on the produce surface [97]. There is a great variety of polysaccharides from diverse sources used for elaboration of edible coatings; among the most common are: chitosan [77], galactomannans [21], pectin [129], alginate [45], carrageenan [55] and starch [104]. Depending on their chemical composition, they are able to: (1) regulate mass transfer processes involving oxygen [4, 81], carbon dioxide [44], water vapor [3], ethylene [44] and other volatile compounds [81]; and (2) have an effect on the mechanical properties of the food [43]. Polysaccharide-based coatings generally exhibit poor water vapor resistance due to their hydrophilic nature; despite of that characteristic some polysaccharides, applied in the form of high-moisture viscous coatings, are able to retard water loss from coated foods [63].

## Composites

The blend of more than one material can lead to the development of composite edible coatings with interesting properties. The usual objective is to take advantage of the maximum possible performance of the blend without changing drastically the properties of their components. Mixtures between different polysaccharides, polysaccharides and proteins and polysaccharides and lipids and waxes are the most studied blends [23, 38, 46, 68, 71, 102].

## Plasticizers

Within the study of coatings, improvement of mechanical and transport properties through the incorporation of other compounds (i.e., plasticizers and lipids) has been a constant subject of interest [12]. Plasticizers have been incorporated to enhance flexibility and resilience of coatings [107] and decrease the presence of cracks and pores [47]. A plasticizer acts by decreasing the intermolecular attraction between polymeric chains, allowing the penetration of polar water vapor molecules [63], highly influencing the final coating permeability. Water, oligosaccharides, polyols and lipids are different types of plasticizers used in hydrocolloid-based coatings [111]. Glycerol is one of the most used plasticizers; it is a hydrophilic molecule (polar) and increasing its concentration causes an increase in water vapor mass transfer. Cerqueira et al. [23] evaluated the influence of glycerol and corn oil on physicochemical properties of galactomannan from *Gleditsia triacanthos* and chitosan-based coatings, and confirmed that the presence of glycerol and corn oil originated a more hydrophilic

structure and a decreased affinity of the coating matrix to water in both polysaccharides, respectively. Olivas and Barbosa-Cánovas [88] carried out a similar study, where the effect of four plasticizers (fructose, glycerol, sorbitol and polyethylene glycol) was evaluated on the mechanical properties and water vapor permeability (WVP) of alginate coatings. These authors reported that the use of plasticizers modified the mechanical properties of alginate coatings, decreasing tensile strength (TS), being this effect more pronounced when RH increases; also, results showed that water acts as a plasticizer in hydrophilic coatings.

## Edible Coatings as Carriers of Bioactive Molecules

The favorable effects of edible coatings on fruits and vegetables (i.e., gas barrier and reduction in metabolic rate) have been extensively proven [41, 85, 113]. Edible coatings have the particularity to act as carriers for a wide range of food additives such as: antioxidants, nutraceuticals, flavoring agents and antimicrobials [93, 101]. Several antimicrobials can be incorporated into edible coatings, including organic acids (e.g., citric, lactic, acetic, benzoic, tartaric, propionic, and sorbic acid), polypeptides (e.g., lysozyme, lactoferrin, natamycin, nisin, and peroxidase), plant extracts and essential oils (e.g., cinnamon, capsicum, garlic, carvacrol, oregano, and lemongrass), mineral salts (e.g., sodium bicarbonate, ammonium bicarbonate, and sodium carbonate), parabenes, oligosaccharides (chitooligosaccharides), among others [89, 96, 98, 118]. These compounds must be considered as GRAS by the corresponding international regulatory agencies in order to be incorporated into edible coatings. Antimicrobials are regulated in the European Union (EU) by the European Commission Framework Directive 1130 [37], while in the USA by the part 21CFR172 [117].

Several authors observed through in vitro studies that the inclusion of antimicrobials into edible coatings enhances the control of rots that cause spoilage in fruits and vegetables. However, more studies of incorporation are necessary to understand how to maintain stable coating properties after bioactive incorporation (e.g., gases barrier, mechanical properties and appearance) [104]. For example, Mohamed et al. [83] evaluated the incorporation of lactoperoxidase system (LPOS), an antimicrobial of broad spectrum, into chitosan coatings at different concentrations (0.5, 1 and 1.5 %); the addition of LPOS showed no significant effect on mechanical properties of the coatings, but led to a bacterial and fungal inhibitory effect depending on chitosan concentration and the strain on *Xanthomonas campestris* pv. *Mangifera indica*, *Colletotrichum gloeosporioides* and *Lasiodiplodia theobromae*. Meanwhile, Ahmad et al. [2] reported that properties of gelatin films from skin of unicorn leatherjacket were affected by the incorporation of bergamot

(BO) and lemongrass oil (LO), resulting in decreases in tensile performance (i.e., tensile strength and elongation-at-break), film solubility and transparency, being WVP also decreased when LO was added. The authors reported higher antimicrobial activity in films incorporated with LO than those with BO, being more effective against Gram-positive bacteria (*Staphylococcus aureus* and *Listeria monocytogenes*) than Gram-negative bacteria (*Escherichia coli* and *Salmonella typhimurium*), but showing no inhibition toward *Pseudomonas aeruginosa*.

Recent works addressed the incorporation of nano-emulsions into edible coatings as a method to disperse lipophilic active ingredients in lower doses and with increased effectiveness. In this context, Acevedo-Fani et al. [1] reported the suitability of nano-emulsions loaded with of EOs (thyme, lemongrass and sage oil) for formation of edible films by microfluidization. The results indicated that physical properties (color, barrier and mechanical) of resulting edible films were influenced by the droplet size and ζ-potential, and were improved for those films including EOs when compared with pure alginate films; furthermore, authors mentioned that antimicrobial activity depends on the composition of EOs and the susceptibility of each particular microorganism to the antimicrobial agent. In that work, edible coatings containing thyme evidenced higher antimicrobial activity against *E. coli*, while films formed from sage oil presented higher transparency, WVP and flexibility than those formed from thyme and LO. Also, Kim et al. [64] demonstrated the stability of emulsions based on carnauba wax and LO was enhanced by forming nano-emulsions using dynamic high pressure (DHP) process. The coatings were applied on grape berries, showing antimicrobial activity against *Salmonella typhimurium* and *E. coli* O157:H7 during storage at 4 and 25 °C for 28 days. The coatings allowed reducing loss of weight, total anthocyanin concentration, antioxidant activity and firmness, and also avoided the degradation of phenolic compounds; while they did not significantly change the flavor of the berries. Salvia-Trujillo et al. [103] evaluated another coating with nano-emulsions based on alginate and LO (0.1, 0.5 and 2 % v/v) and compared its effect with conventional coatings on the safety and quality attributes of fresh-cut Fuji apples during cold storage. Edible coatings with LO droplets in nano-size showed a better inactivation of *E. coli* than conventional emulsions. Higher LO concentration (0.5 or 1 % v/v) allowed significant browning, but not on those coated with 0.1 % (v/v) of LO. Also, the respiration of fresh-cut apples was reduced when increasing concentration of LO, but droplet size showed no significant influence on the quality parameters.

Incorporation of antimicrobial agents into edible films allows using small antimicrobial concentrations and low diffusion rates; then their activity can be prolonged during produce distribution, transport and storage. However, it is important to modulate the release rate and migration of antimicrobial compounds from the edible coating matrix. The use of release kinetics models allows estimating optimal active agent concentrations during postharvest storage periods; an example is reported by Del Nobile et al. [30], which determined that Fick's second law properly describes the release kinetics of thymol from zein films at 5, 10, 20 and 35 % (weight of thymol/weight of dry polymer) and that thymol diffusion coefficient is independent from thymol concentration. Some examples of antimicrobial edible coatings showing efficiency on the control of rot pathogens of several fruits and vegetables are presented in Table 2.

## Edible Coating Selection and Application

Successful application of coatings depends on the selection of the adequate method, which can be chosen between dipping, brushing, spraying and panning [128]. These procedures can be selected based on surface characteristics of the produce and the main purpose of the coating. The most common coating procedure implies wetting the produce by the coating mixture followed by an adhesion process, where the penetration of the solution into the produce's skin occurs [58]. The wetting phase (governed by the surface's spreadability) is crucial, because if the affinity of the coating for the produce is optimal, the time required for this operation is minimal allowing virtually spontaneous spreading of the coating solution [82].

Before deciding on coating application, it is necessary to take into account the two ripening patterns of the produce (climacteric and non-climacteric), in order to select the optimal coating in each case. Climacteric fruits (e.g., tomato, banana, avocado and apple) are characterized by increased respiration and ethylene production rates during ripening. The harvest of this type of produce is recommended as soon as possible, once its physiological maturity is reached. Nevertheless, they ripen rapidly during transport and storage; thus, some of the challenges are to prevent ripening by slowing down respiration and preventing dehydration. Application of coatings able to reduce the ethylene production rate and to control gas exchange ($CO_2/O_2$) is a possibility for postharvest control of climacteric fruits, in such a way that they can delay the maturing process [7]. Adequate coatings for this kind of fruits are those based on blends of polysaccharides, proteins and/or lipids, since blends can allow overcoming deficiencies of particular components. For example, blends of polysaccharides and additives (e.g., glycerol and lipids) can improve the permeability to gases and water vapor transfer when compared with polysaccharides alone [23]. Lima et al. [71] reported the effectiveness of galactomannan–

**Table 2** Examples of applications of antimicrobial edible coatings in fruits and vegetables

| Matrix | Antimicrobial agent | Microorganisms target | Fruit/vegetable | References |
|--------|---------------------|----------------------|-----------------|-----------|
| Hydroxypropyl methylcellulose and beewax | Ammonium carbonate | *Botrytis cinerea* | Cherry tomatoes | Fagundes et al. [39] |
| Pullulan | Sweet basil extract | *Rhizopus arrhizus* | Apple | Synowiec et al. [112] |
| Chitosan | Lemon essential oil | *Botrytis cinerea* | Strawberry | Perdones et al. [91] |
| Gum arabic | Cinnamon oil | *Colletotrichum musae* and *Colletotrichum gloeosporioides* | Banana and papaya | Maqbool et al. [75] |
| Mesquite-based gum | Thyme and Mexican lime essential oils | *Colletotrichum gloeosporioides* and *Rhizopus stolonifer* | Papaya | Bosquez-Molina et al. [13] |
| Chitosan | Grapefruit seed extract | *Botrytis cinerea* | Redglobe table grapes | Xu et al. [125] |
| Chitosan | Calcium chloride | Decreases the microbial growth rate (fungi and bacteria) | Strawberries | Ribeiro et al. [100] |

collagen blends in reducing $O_2$ consumption rate by 28 % and $CO_2$ production rate by 11 % when compared with uncoated mangoes, and both rates by 50 % when compared with uncoated apples, respectively.

In non-climacteric fruits (e.g., citrus, pineapples, strawberry and grapes), respiration shows no dramatic change and ethylene is not required for fruit ripening [50], being the losses mostly related to weight loss during transportation. For non-climacteric fruits, it is a common practice to apply lipid-based coatings (e.g., waxes and resins) where the low permeability to $CO_2$, $O_2$ and water vapor allows reducing metabolic rates and water loss, while also providing an attractive appearance to the produce [7]. Nevertheless, excessive restriction of gas exchange sometimes occurs in waxed fruits, leading to undesirable flavor changes [8, 53, 114]. Blends of lipids and polysaccharides can be used instead to provide appropriate gas and moisture barrier [92]. Furthermore, it has been demonstrated that when polysaccharides solutions are applied at higher concentrations (e.g., chitosan), respiration can be reduced together with changes in weight loss, firmness and external color in strawberry fruits [57].

In addition to the issues mentioned above, in both cases (climacteric and non-climacteric fruits), it is important to take into account temperature control, due to the impact that it shows in fruits' respiration rate. In fact, respiration rate significantly increases or decreases when temperatures are increased or decreased, respectively. This temperature effect must be taken into consideration since even coatings built for ideal storage temperatures can cause anaerobic fermentation and physiological disorders [7] if respiration rates are significantly changed.

Different formulations of edible coatings are available commercially; examples of products well-known in the market are:

1. NatureSeal® (Mantrose-Haeuser, Co., Inc., Westport, CT, USA). Based in ascorbic acid, calcium chloride, hydroxypropyl methylcellulose, it inhibits enzymatic browning, maintains taste, texture, and color of fresh-cut fruits and vegetables;

2. Pro-long™ or TAL Pro-long™ (Courtaulds Ltd., Derby, United Kingdom) is an aqueous dispersion of sucrose polyesters of fatty acids and sodium salt of carboxymethylcellulose; it modifies the internal atmosphere of the fruit and maintains its natural color;

3. Semperfresh™ (Agricoat Industries Ltd., Seattle, WA, USA) is a mixture of sucrose esters of short-chain unsaturated fatty acids and sodium salts of carboxymethylcellulose; it is a coating developed for the postharvest protection of fruits such as melons, pears, pineapples or cherries;it allows reduction in the respiration rate, ripening, weight loss and conserves the natural color of fruits [5].

New promising natural products have been recently introduced such as:

1. Clarity Citrus (Fagro Post Harvest Solutions S.A. DE C.V., Ramos Arizpe, Mexico), composed of polyethylene, shellac and carnauba; it is specially formulated for citrus fruits at postharvest stage and acts reducing gas exchange, the ripening process and water loss;

2. Naturcover (Decco Ibérica Post Cosecha S.A.U., Valencia, Spain), based on sucrose esters of fatty acids and other additives; it is an edible coating that reduces weight loss and chilling injury in stone fruit, and delays ripening in apples and pears. It also reduces stains of scratches on pears and maintains freshness in citrus fruits;

3. Foodcoat Fr Drencher DMC (Domca S.A.U., Granada Spain) is formulated from oil acids derivates; it acts reducing the respiration rates of some fruits and vegetables, diminishes fruit weight loss and retards ripening. It also helps enhancing natural brightness and maintaining fruit consistence [86].

## Emerging Technologies: Development of Nano-laminate Coatings

Edible coatings can be considered an effective postharvest technology for extending shelf life of fruits and vegetables. However, their application still faces a number of disadvantages since: (1) they can impart off-flavors associated with the flavor of coating materials and to their deterioration (e.g., rancidity of lipids); (2) they may have their own color and be possibly unattractive for consumers; (3) they can provide an undesirable tacky consistence; (4) it is difficult to obtain an adequate homogeneity for each produce surface being necessary to optimize the application and the drying step conditions; and (5) despite being good carriers of bioactive agents, coatings can require large amounts of those compounds in order to reach optimal effectiveness, and sometimes this incorporation presents difficulties.

All of these problems have been studied in the last years, being the solutions presented in most of the cases based in the use of new emerging technologies. One of the examples is the use of nanotechnology. Nanotechnology uses materials at nanoscale ($\leq$100 nm), exploiting differences in physicochemical properties exhibited by these materials when compared with those at a larger scale [51]. It represents a new tool for food technologists in the food packing area by promising packaging materials that will guarantee food products with a longer shelf life, maintaining their safety and quality [87].

On the other hand, one technique that explores the nanoscale advantages is Layer-by-Layer (LbL) deposition which can be used for nano-laminate coatings formation. It consists in the use of two or more layers of, e.g., oppositely charged materials with nanometer dimension (1–100 nm per layer) that are physically or chemically bound to each other and are assembled layer-wise on core materials [29, 69, 127].

The LbL technique is quite simple and enables using a wide range of materials (e.g., proteins, polysaccharides, lipids, and nanoparticles). These materials are able to interact either by electrostatic interactions, hydrogen bonding, covalent bonds, complementary base pairing and hydrophobic bonding. Moreover, depending on the template used (e.g., planar and colloidal), it is possible to design a variety of nano-laminate systems including nano-emulsions, nano-films and nano-capsules [22].

The resulting properties of nano-laminate coatings such as mechanical properties, gas permeability and swelling and wetting characteristics are influenced by the kind of adsorbing materials utilized and also by the sequence, the total number of layers and the conditions used for preparation (e.g., temperature, pH and ionic strength) [123]. This leads to a great number of possibilities, thus allowing tailoring the final properties of the coating in order to ensure the desired functionality.

One of the advantages of these nano-systems is their gas barrier properties when compared with conventional edible coatings. Table 3 shows the permeabilities to oxygen and water vapor of conventional and nano-laminate coatings. It is suggested that barrier properties of nano-laminate coatings are improved due to their nano-structure, which has an increased tortuosity resulting from the electrostatic interactions between the nano-laminate's components and also from the interpenetration of the successively deposited layers that hampers gas molecules migration through the structure [61, 79, 94]. The application of LbL technique in fruits and vegetables is very recent, and few studies showed its effect on shelf-life parameters. One of the first steps in the application of LbL technique in produce is to prove its success (by means of microscopy techniques and/or contact angle measurements). Figure 2b shows a nano-laminate

**Table 3** Water vapor (WVP) and $O_2$ permeabilities ($O_2P$) values of conventional edible coatings and nano-laminate coatings

| Composition | Type | WVP $\times 10^{-11}$ $(gm^{-1}\ s^{-1}\ Pa^{-1})$ | $O_2P \times 10^{-14}$ $(gm^{-1}\ s^{-1}\ Pa^{-1})$ | Thickness ($\mu$m) | References |
|---|---|---|---|---|---|
| Starch | Coating | 17.7 | ND | 69.2 | Garcia et al. [48] |
| ι-carrageenan | Coating | 11.80–235[a] | 720 | 50 | Hambleton et al. [54] |
| Chitosan | Coating | 8.60 | 0.71 | 50 | Fajardo et al. [40] |
| Alginate and chitosan | Nano-laminate | 0.85 | ND | 0.12 | Carneiro-da-Cunha et al. [19] |
| κ-carrageenan and chitosan | Nano-laminate | 0.020 | 0.043 | 0.342 | Pinheiro et al. [94] |
| Pectin and chitosan | Nano-laminate | 0.019 | 0.069 | 0.266 | Medeiros et al. [79] |

*ND* not determined

[a] Depending on temperature and humidity gradient
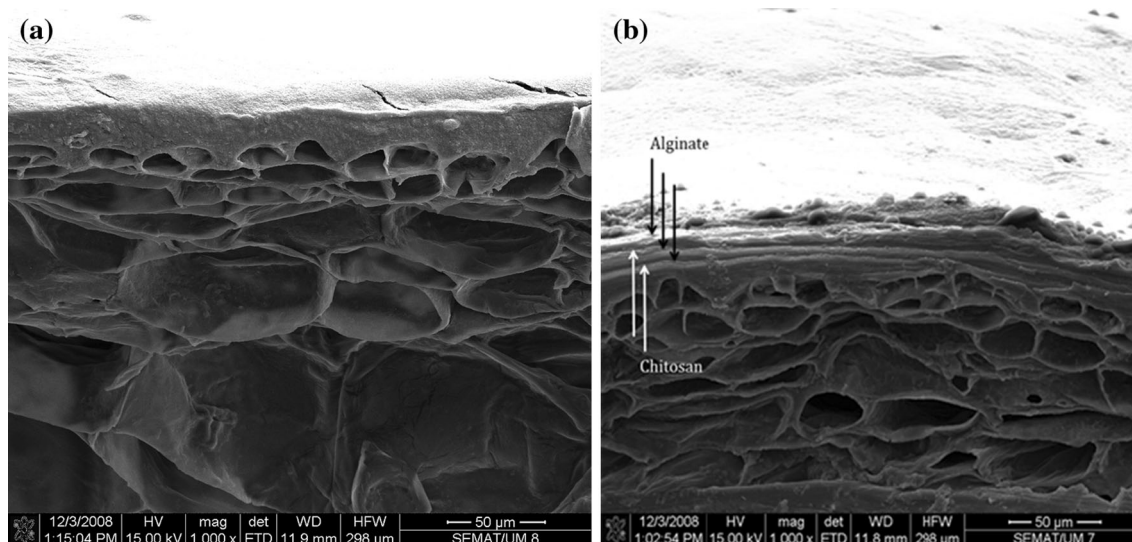
Fig. 2 Scanning electron microscopy images of the mango surface (a) and of nano-laminate coating on mango surface (alginate/chitosan/alginate/chitosan/alginate) (b)

coating on mangoes surface by means of scanning electron microscopy (SEM; Fig. 2) where it is clear the alternate deposition of alginate and chitosan on mangoes' surface when compared with mango without nano-laminate coating (Fig. 2a).

Application of coatings or waxes at industrial level is typically conducted by micro-spraying using specific nozzles with a bed of propylene brushes or by direct immersion of the food products. The products go through a washing and disinfection step (most cases), being perfectly dried before the coating step. For the application by spraying, the products are rotating while the coating/wax is adhered to the surface. Drying steps can be performed in a tunnel with strong ventilation (40–45 °C) between 1.5 and 2.0 min or at room temperature. As far as we know, nano-laminate coatings have not been applied at industrial level. In our opinion for a successful application of nano-laminate coatings, the immersion method should be used with washing (in water) and drying (at temperatures around 30 °C with strong ventilation) steps between layer applications. The times for this process as evaluated at laboratory scale are around 10–20 min, but a re-evaluation/adaptation is necessary in order to be applied at industrial scale. It is important to mention that there are studies referring the possibility of using spraying in the development of multilayers [106].

Recent works showed successful applications of nano-laminate coatings in commodities describing the application conditions, such as number of layers, immersion time, washing and drying steps. Medeiros et al. [79] evaluated a nano-laminate coating based on five layers of pectin and chitosan (at a concentration of 0.2 %, w/v) on whole

"Tommy Atkins" mangoes applied by immersion of 15 min into each polyelectrolyte solution and a washing procedure with distilled water at pH 7.0 and 3.0 for pectin and chitosan, respectively. After 45 days, the coated mangoes presented better appearance, reduction in water loss, and absence of fungal growth that uncoated mangoes; also, reduction in gas flow was observed, as a result the shelf life of mangoes was increased. Moreover, Medeiros et al. [80] reported the positive effect on shelf-life extension of Rocha' fresh-cut pears (CP) and whole pears (WP) upon application of a nano-laminate coating composed of five layers of κ-carrageenan and lysozyme (each at concentrations of 0.2 %, w/v). The immersion time into each polyelectrolyte solution was 5 and 15 min for CP and WP, respectively, and subsequently rinsed with deionized water with pH 7.0 (κ-carrageenan) and pH 3.8 (lysozyme). The coating avoided mass loss of CP, proving the efficiency of the nano-laminate as water loss barrier. Total soluble solids values were lower for both coated CP and coated WP during the experimental period (7 and 45 days, respectively); while low values of titratable acidity for coated CP and WP were an indicative of the delay in maturation process associated with the reduction in gas exchange ($O_2$ and $CO_2$) by the application of the coating. More recently, Souza et al. [109] studied a nano-laminate coating based on five alternate layers of alginate and chitosan (each at concentrations of 0.2 %, w/v) to extend the shelf life of fresh-cut mangoes stored under refrigeration (8 °C) for 14 days. Polyelectrolyte solutions were applied by immersion for 15 min and subsequently rinsed with deionized water with pH 7.0 and 3.0 for alginate and chitosan, respectively. An additional drying step with flow of

nitrogen at 25 °C for 15 min was used between layers. Lower values of soluble solids, mass loss and higher titratable acidity were observed on coated fresh-cut mangoes. Moreover, the nano-laminate allowed the reduction in malondialdehyde content (an indication that the coating application prevents senescence). According to microbial analyses, the shelf life of fresh-cut mangoes was increased up to 8 days at 8 °C when compared with uncoated fresh-cut mangoes (<2 days).

Nano-laminate coatings are able to incorporate functional compounds under the form of nanoparticles, which presumably have greater chemical reactivity and can be more bioactive than larger particles as their size has better access to any structure [73]. Furthermore, nanoparticles can have a dual purpose: besides acting as carriers of additives, they may also provide improvements in the mechanical and barrier properties of the structures where they can be incorporated. However, the efficiency of nano-layer systems with a variety of features (e.g., antioxidant, antimicrobial and reduction in gas exchange) still remains little studied.

The use of LbL technique has also been studied at microscale; some examples are reported by Brasil et al. [16]. In this work, a microencapsulated beta-cyclodextrin and trans-cinnamaldehyde complex (2 g/100 g) was incorporated into a laminate coating made of chitosan and pectin; the quality of fresh-cut papaya was extended to 15 days at 4 °C while uncoated fruits could not reach this far (<7 days). The coating reduced the losses of Vitamin C and total carotenoids content; in addition, the encapsulation of trans-cinnamaldehyde was successful, since it had no negative impact on the fruit's flavor. In another work, Mantilla et al. [74] evaluated the efficacy of a microencapsulated antimicrobial complex (beta-cyclodextrin and trans-cinnamaldehyde) incorporated into a laminate coating composed of pectin–alginate on fresh-cut pineapples. The system showed microbial growth inhibition, while the original qualities (color, texture and pH) of pineapples were kept and the shelf life was extended to 15 days at 4 °C.

## Conclusion

One of the major causes of postharvest losses in fruits and vegetables worldwide is the lack of postharvest technology solutions in developing countries. One of the solutions is the application of edible coatings, where nano-laminate coatings showed in the last years to be one of the promising technologies to increase fruits shelf life. Despite the promising results is still needed an appropriate optimization and implementation of these technologies, in order to be effectively used in the processing chain of fruits and vegetables.

The use of nanotechnology promises a great impact in food and agriculture industries. Nanotechnology advanced not only in packaging technologies, through the development of nano-laminate and bioactive nano-laminate coatings for application on fruits and vegetables, but also in the design of biosensors to identify and quantify diseases, residuals of agrochemicals, modification of food composition, and in the nano-formulation of agrochemicals to control pests and application of fertilizers. However, optimization and implementation of these technologies still faces some challenges, e.g., difficulty measuring the nano-laminate coatings' thickness (nanoscale); and industry viability, due to the changes needed in packing-houses for the application of nano-laminate coatings.

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