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Recent Trends in Edible Films and Coatings for Fresh and Minimally Processed Fruits

Siddharth Agarwal
Department of Pharmaceutical Sciences and Technology, Institute of Chemical Technology, Mumbai
Prachi Mittal
Department of Polymer and Surface Engineering, Institute of Chemical Technology, Mumbai

Abstract:
In the last decade, a lot of interesting work has been done to develop novel films and coatings as food packaging materials which enhance foodquality and safety during storage. Recent research efforts have been centralized on designing edible coatings based on biodegradable polymers which would not only serve the requirements of packaging but also solve the issue of by-products of the food industry by utilizing them into film-forming components. Originally intended to minimize water loss and delay aging of coated fruits through selectively allowing gaseous interactions, coatings have evolved to meet the requirements of controlled release of integrated vitamins, nutraceuticals, antimicrobial agents and antioxidants, which is demanded by the food industry. New technologies such as layer-by-layer assembly and nanoencapsulationhave given promising results. This review investigates the materials used in formulation of coatings which are available presently and also attempts to discuss the recent advances made in that subject.

Keywords: *Edible coatings, biodegradable polymers, layer-by layer assembly, nanoencapsulation*

1. Introduction

The edible coatings are defined as thin layer of material that covers the surface of the food and can be eaten as part of the whole product(Guilbert, Gontard, & Cuq, 1995). It is one of the most recent developments in field of food packaging. Edible coatings areeco-friendly and biodegradable technology that can be applied to food products to control moisture transfer, gas exchange or oxidation processes. It is one of the most novel techniques to extend shelf-life and improve quality of fresh and minimally processed fruits(Hyun Jin Park, 1999).

One major advantage of using edible films and coatings is that several active ingredients can be incorporated into the polymer matrix and consumed with the food, thus enhancing safety or even nutritional and sensory attributes. Also, use of this technology reduces the synthetic packaging waste, though some packaging is required on edible coating from point of hygiene and handling.

Conventionally, the properties of coatings are first characterized when they are cast and then peeled off from a plate. However coating properties are affected by the interaction between coating and fruit surface, thus characterization of films after being coated on fruits is essential and critical.

This paper reviews some of the most recent advances in the application and development of edible coatings for fresh and minimally processed fruits, discussing wide range of compounds that can be used in the formulation of edible coatings depending on target application, the available and potential techniques to characterize coated commodities. We have also tried to briefly account for advanced studies, focussing on the development of new technologies that allow for a more efficient control of coating properties and functionality, and incorporation of nutritional and anti-microbial ingredients to the coatings.

2. Constitution of Edible Coatings for Fresh and Minimally Processed Fruits and Vegetables

A coating must meet many demands of legality, safety and performance. During storage it must not ferment, coagulate, separate, develop off flavours or otherwise spoil. It is requires of the coating the properties of spreading evenly, drying quickly, not foaming and ease in removing from equipment. Once applied it should not crack, peel off during handling and storage or decolour. It is essential that it should exhibit selective permeability of gases, such as oxygen, carbon di oxide and water vapour and at the same time it should not completely stop permeability as it would result in anaerobic fermentation.Materials used for making coatings are discussed below.

2.1. Polysaccharides

Polysaccharides are the most commonly used edible coating for fruits and they are present in a wide range of commercially available formulations(Kester & Fennema, 1986)

Although polysaccharides are highly hydrophilic and show considerable amount of permeability to water vapour, they exhibit effective gas barrier properties. Variations in the molecular characteristics such as molecular weight, hydrophobicity, charge and degree of branching affect their physicochemical properties and their ability to form coatings and their performances. Generally polysaccharide based coatings are not used for samples intended to be kept immersed in solutions, such as juices or in a high relative humidity environment as they are water soluble. To make the coatings insoluble, cross linking treatments in presence of monovalent and divalent ions can be employed. Main polysaccharides that are used as edible coatings are cellulose based, starch based, alginate based, chitosan based and carrageenan based(Krochta & De Mulder-Johnston, 1997).

Cellulose is the world's most abundant polysaccharide which is the major component in plant cell walls and also contained in cell walls of algae as well as membranes. Its principle chains are linear β - (1→4)-D-glucopyranose. Although many varieties of cellulose derivatives are available, only a few of the cellulose ethers find application in foodstuffs(Majewicz, Erazo□Majewicz, & Podlas, 2003). These are generally hydroxypropyl methylcellulose (HPMC), methylcellulose (MC), hydroxypropylcellulose (HPC), ethylmethylcellulose (EMC) and sodiumcarboxymethylcellulose (CMC). Some of their physical and chemical properties such as water retention, sensitivity to electrolytes and other solutes, dissolution temperatures, gelation properties, and solubility in non-aqueous systems can be altered by changing the level of carboxymethyl, methoxyl and hydroxypropyl substitutions(Baker, Baldwin, & Nisperos-Carriedo, 1994).

Nonionic water-soluble ethers such as MC, HPMC, and HPC have very good film-forming properties for edible coatings. They yield water soluble but tough and flexible transparent films that are resistant to fats and oils. MC films are the least hydrophilic of the cellulose ethers and produce films with relatively high water vapor permeability. This is because MC films are tough and flexible, while the internal plasticizing effects of the high level of hydroxypropyl substitution in HPC result in a film of lower tensile strength and greater elongation. This is because thermal gelation in MC is higher because, as the methyl concentration increases, the gels formed on heating become firmer whereas hydroxypropyl groups tends to make them weaker and increase the temperature at which gelation occurs(Brownsey & Ridout, 1985).

Chitosan is a biodegradable biocompatible polymer derived from natural renewable resources of crabs and shrimps and is the second most abundant polymer in nature after cellulose, with numerous applications in various fields, and one of which is the area of edible films and coatings. Chitosan is the chitin derivative produced by the N-deacetylation process, resulting in the amino group at C-2 position on its backbone. Chitosan has antibacterial and antifungal properties which qualify it for food protection, however, its weak mechanical properties, gas and water vapor permeability limit its uses.

Chitosan film is usually prepared by casting chitosan solution on a certain plate. Since chitosan is only soluble in acidic conditions, the type of organic acid used is crucial to the mechanical properties of chitosan films(Harish Prashanth & Tharanathan, 2007). Acetic acid have been considered as a common solvent for chitosan, but it was reported that acetic acid resulted in brittle coatings as they had low elongation rate and higher tensile strength when compared with other organic acids, such as malic, lactic and citric acid(Krajewska, 2004).

It was shown that more flexible films with lower tensile strength and higher elongation rate can be produced by incorporation of gelatin in chitosan film. The more gelatin ratio included in the film resulted in more translucent film due to the reduced light transmission. The translucent appearance of the film will greatly expand chitosan-based active film applications as edible coating(GHAOUTH, Arul, Ponnampalam, & BOULET, 1991).

Starch is a natural polysaccharide, a mix of amylose and amylopectin and is the most commonly used one in the edible coating manufacture as abundant, biodegradable, inexpensive and easy to modify as per requirement. Unmodified starches have very limited use in the food industry because raw starches do not possess the required functional properties as demanded by processors.Native starch can be converted into a thermoplastic material in the presence of plasticizers, such as water and glycerol by conventional methods(Thiré, Simão, & Andrade, 2003).This improves the film flexibility and extensibility(Mali, Grossmann, Garcia, Martino, & Zaritzky, 2002). Modification of native starch can also be achieved by disruption of their hydrogen bonding through reduction of molecular weight or chemical substitution, which in turn leads to lower gelatinization temperatures and reduced retrogradation. Starch hydrolysis by acid treatment shortens the length of the amylose chains and converts the branched amylopectin into linear amylose units, which enables it to become dispersed at higher concentrations than unmodified starch.

Alginates and carrageenans can also be used to prepare edible coatings. Alginic acid is a high molecular weight polysaccharide consisting of varying proportions of D-mannuronic acid and L-guluronic acid and alignates are salts of these. Alginates' gel-forming properties are mainly due to their capacity to bind a number of divalent and trivalent ions like calcium, magnesium, which are added as gelling agents make them suitable for films(Cha & Chinnan, 2004). Carrageenan is a complex mixture of several polysaccharides. The three main commercial carrageenans are ι-, κ-, and λ-carrageenan, whose names specify the major substitution pattern present in their galactan backbone. Film formation of carrageenan based polymers includes gelation mechanism during moderate drying, leading to a three-dimensional network formed by polysaccharide double-helices and to a solid film after solvent evaporation(Karbowiak, Debeaufort, & Voilley, 2007).

2.2. Proteins

Proteins are molecules with specific amino acid sequences and molecular structures. The structural and functional diversity of protein is mainly due to wide variation in substituent (side chains) attached to α carbon of amino acids. Depending upon sequential order of amino acids, the protein will assume different structure along polymer chain which will determine the secondary, tertiary and quarternary structures. These structures can be easily modified to optimize protein configuration, protein interaction and resulting film properties. Also proteins may vary in their molecular weights, conformations (globular, random coil, helix), electrical characteristics (charge versus pH), flexibilities (rigid versus flexible), and thermal stabilities. The ability to form coatings and characteristic properties of the coating formed is thus determined by the difference in molecular characteristics which are in turn dependent on their biological origin and function. Proteins from both plant and animal origin can be used in the formulation of edible coating for fruits .Edible protein film-forming material derived from animal sources include, casein and whey protein, collagen, gelatin, myofibrilar protein and egg albumin and those obtained from plant sources are corn-zein, wheat gluten, soy protein, peanut protein, and cotton- seed protein , peanut ,rice , pea, pistachio grain sorghum (Gennadios, 2002).

Casein,derived from milk based edible coating shows high nutritional quality, excellent sensory properties, and good potential, for providing food products with adequate protection against their surrounding environment. Also plasticisers can be used to further enhance and optimize the properties of edible coatings.Lactic acid casein films plasticized with sorbitol has exhibited better mechanical and barrier properties(Chick & Ustunol, 1998).

Whey protein, a mixture of proteins with diverse functional properties, is used in making films by denaturation of whey protein in aqueous solution. With the addition of plasticizer, heat-denatured whey proteins produce transparent and flexible water-based edible coatings with excellent oxygen, aroma, and oil barrier properties at low relative humidity. However, it has poor moisture barrier than wheat gluten, soy protein, casein and zein films due to hydrophilic character of whey protein. Incorporation of lipid materials improves film moisture barrier properties by increasing hydrophobicity. WPI lipid composite film can be accomplished by laminating the protein film with lipid layer. The degree of protein denaturation and unfolding as heating time and temperature increase affects the degree and nature of protein-protein crosslinking and as the consequence solubility and mechanical properties of the film(E. A. Baldwin, Hagenmaier, & Bai, 2011).

Proteins insoluble in water such as corn zein and wheat gluten are used to produce insoluble coatings, whereas water soluble proteins produce coatings of varying solubility, depending on the protein and the conditions of coating formation and treatment(Krochta, 2002).

Also protein solubility depends on the pH, so it should be considered during formulation and application of coatings. The solubility becomes insignificant in case of denatured proteins.

2.3. Lipids, Waxes and Resins

Lipid-based edible coatings are hydrophobic and are employed to reduce moisture loss(E. A. Baldwin et al., 2011). This has a very important use in food industry as there is a crucial requirement to control the desiccation of fresh fruits and vegetables(Morillon, Debeaufort, Blond, Capelle, & Voilley, 2002). Waxes are the most common lipid used in coatings. Waxes such as beeswax, candelilla wax, carnauba wax, triglycerides, acetylated monoglycerides, are incorporated into so as to impart hardness, luster and increase melting point.

Resins are a classified as a group of acidic substances that are usually secreted by specialized plant cells into long resin ducts in response to injury or infections in plants. Shellac, which is the secretion by the insect Lacciferlacca is the most commonly used resin in coatings for fresh fruits, pharmaceuticals and jelly bean. This resin is soluble in alcohols and in alkaline solutions and is compatible with most waxes, thus it can be used for improving moisture barrier properties and imparting glossy finish.

3. Properties and Characterization

The research is being carried out on use of edible coatings, to increase their shelf-life which depends on the mechanical and barrier properties of the films formed. Also these coating can be a way to supply essential proteins to the body, which are not generated in sufficient quantity in human body.

The effectiveness and functionality of each coating depends on their physicochemical and barrier properties, which are very often closely related to its microstructures. The coating properties are affected by the topography of the surface offruit during its application. Also the effect of coating on physiological and morphological properties of the fruit is to be accounted. So it is important to characterize coating before and after it is coated on the fruit.

In this paper we briefly discuss the most important properties of the coating films, and name their characterization methods.

Thickness and Microstructure of the edible coatings is directly related with some important properties such as permeability to gases. The coatings that are obtained by casting and drying on levelled plates can be peeled off and their thickness can be easily measured by using a hand-held micrometer. But, it is difficult to measure the thickness of coatings accurately once they have been applied to the fruit surface. In these cases, an estimation of the coating thickness can be obtained by means of the quantification of the surface solid density, SSD(Vargas, Albors, Chiralt, & González-Martínez, 2006; Villalobos, Hernández-Muñoz, & Chiralt, 2006). Spectroscopic ellipsometry is another technique which can be possibly used to determinethe thickness of the coating. Though, it has not been used till now for edible coating(Schram, Terryn, & Franquet, 2000). Also by using Scanning Electron Microscopy, Atomic Force Microscopy and other microscopy techniques, the surface roughness, topography of coated fruits and coating thickness can be characterized as well(Hershko & Nussinovitch, 1998). The properties permeability to gases and resistance to water vapour transmission of the coating is better characterized by analysis of coating microstructure.

Water vapour resistance: - In order to determine if the coating shows the required properties for a specific combination of storage conditions, it is very important to directly measure the product's permeability to water vapour exchange under controlled environmental conditions(Amarante & Banks, 2001). Hence, by monitoring the weight loss of samples at a controlled temperature and under controlled relative humidity conditions, the water vapour resistance (WVR) of coated fruits can be obtained.

The gas permeability of coatings can be evaluated by measuring the internal composition of coated fruits, generally in terms of concentration of O2 and CO2, and also some important volatile compounds such as ethanol and acetaldehyde, which governs the metabolism of coated fruits. The respiration rate of the coated fruits can be determined by measuring the changes in its internal composition.It is noteworthy that their mechanical properties are influenced by the changes in the internal atmosphere of coated fruits and the subsequent delay in their metabolism.

Appearance: Color, opacity and gloss of edible coatings are important properties, so as to ensure consumer approval, can be measured by means of colorimeters, and glossmeters respectively.

The parameters such as surface free energy , the interfacial tension between surface of fruit and coating solution , and contact angle determine the amount of liquid that adheres to the surface and hence , the final thickness of the film on the fruit(Wong, Gastineau, Gregorski, Tillin, & Pavlath, 1992).

The most crucial factor is that the coatings shouldhave negligible effect on the sensory quality of coated fruits in terms of colour, gloss, basic tastes (bitterness, sourness, and sweetness), aroma and firmness. Sensory attributes of the coated fruits should not be compromised because of the coating films as it can adversely affect consumer acceptability(Eswaranandam, Hettiarachchy, & Meullenet, 2006; Han, Lederer, McDaniel, & Zhao, 2005).For example, colour and gloss are adversely affected due to incorporation of lipids into coatings(Tanada-Palmu & Grosso, 2005).

4. Future Trends

The present day research in field of edible coating is focused on to develop technologies that ensure more precise control of coating properties and functionality. Most of these new methodologies are based on composite or multilayered systems. Although these technologies are yet not practically applied on food products, stores a vast potential for future.

The layer-by-layer (LbL) electro deposition to develop multilayered coatings is one of the methods(Weiss, Takhistov, & McClements, 2006).The incorporation and controlled release of vitamins and other functional or antimicrobial agents can be achieved by engineering multilayered coatings with desired functional properties. A possible multilayered structure could include three layers: a matrix layer (e.g. based on biopolymer like alginate, chitosan etc) that contains the functional substance; an inner control layer that regulates the diffusion rate of the functional substance by ensuring its controlled release; and a barrier layer that controls the permeability to gases and prevents the migration of the active agent from the coated food(Gennadios, 2002).

Micro and nanoencapsulation is defined as a technology for packaging solids, liquids, or gaseous substances in miniature (micro and nanoscale), sealed capsules that can release their contents at controlled rates under specific conditions is another promising technique which can be used to incorporate functional ingredients and antimicrobials into edible coatings for fruit. The release can be signalled by pH variation, temperature, irradiation, or osmotic shock. Encapsulation of materials enhances their stability and simplifies maintenance, thus protecting them from moisture, heat, or other extreme conditions.

The use of this technique is increasing in food industry as it's a very feasible way to incorporate enzymes ,pro- and prebiotics and other ingredients that add value to the food products, as well as functional ingredients that are very susceptible to lipid oxidation such as omega-3-fatty acids(Lopez-Rubio, Gavara, & Lagaron, 2006).

Composite films is another attractive area of research as composites consist of both hydrocolloids and lipids so as to take advantage of special functional characteristics of each group, and eliminating drawbacks poor mechanical properties of only lipid based coating (Donhowe & Fennema, 1994). Generally, lipids plays major role in enhancing the water vapor resistance whereas hydrocolloids ensure selective permeability to O2 and CO2, other volatile compounds like ethanol and acetaldehyde, and also improves mechanical properties(Arvanitoyannis, Nakayama, & Aiba, 1998).

Composite coatings can be created by the subsequent deposition of different layers (multilayered coatings) or can be made by the deposition of a single layer of material. Bilayer coatings are formed by first casting and drying the layer of polysaccharide or protein, and then applying lipid layer(Debeaufort, Quezada-Gallo, Delporte, & Voilley, 2000).As an example, Debeaufort et al. developed bilayers by adding a mixture of lipids (paraffin oil, paraffinwax, or a mixture of hydrogenated palm oil and triolein) onto a methylcellulose layer(Wong, Tillin, Hudson, & Pavlath, 1994). Wong et al. coated apple cubes with double layers of polysaccharides (cellulose, carrageenan, pectin, or alginate) and acetylated monoglyceride.

Finally, the most recent approach to improve coating properties is to make nanocomposites by incorporating nanosized clay materials such as layered silicates into biopolymer based matrices. The composites with better mechanical, water vapour barrier, and antimicrobial properties than the traditional chitosan coatings can be achieved incorporating different nanoparticle (montmorillonites, nano-silver, and silver-zeolite) into chitosan matrix(Rhim, Hong, Park, & Ng, 2006). However, even if these studies seem to be promising, the greatest obstacle that lies in path of the scientific community when incorporating these nanomaterials into edible coatings or food is the lack of research and trials into their possible toxicity.

5. Applications

The quality of fresh and minimally processed fruits can be greatly enhanced by using edible coating technologies which makes it possible to precisely control gas permeability, texture, and color changes in fruits by means of quantitative or qualitative changes in coating formulation.

Depending upon mechanisms involved like controlled moisture transfer between the fruit and the surrounding environment, the controlled release of antimicrobial substances, antioxidants; incorporation of nutritional ingredients , the reduction of the partial pressure of internal oxygen with a decrease in fruit metabolism, various edible coatings formulations technologies are available and are being developed(Shahidi, Arachchi, & Jeon, 1999).

For example proteins and polysaccharides coatings, whether mixed with lipids or not, present the best CO2 and O2 permeation ratio. The application of corn zein coatings on tomatoes or sucrose polyester on apples has been observed to delay colour, weight, and firmness changes(H. Park, Weller, Vergano, & Testin, 1993; Hyun J Park, Chinnan, & Shewfelt, 1994).

The shelf-life can be increased by incorporating antimicrobial agents within the film. Foreg. chitosan coating which is a well-known natural antifungal agent with selective barrier properties to gases and water vapour, when coated on the strawberries or raspberries are observed to prevent water loss via transpiration and enhances respiration(GHAOUTH et al., 1991). Cellulose derivative coatings on nuts, almonds, hazelnuts, and peanuts protect them against oil migration and oxidation. The coatings made from wax, cellulose derivatives, starch, pectins, and/or proteins can possibly to reduce moisture loss and prevents spoilage and sometimes rancidness in fruits (grapes, guavas, mangoes etc.)

Another advantage of edible coatings is observed when applied to minimally processed (MP) fruits, that is fruits which have been cut, peeled and/or slightly processed to be ready to eat having quality and freshness equivalent to the fresh product, still having living tissues(Khwaldia, Perez, Banon, Desobry, & Hardy, 2004). Some examples of the application of these coatings to MP fruits include Carrageenan glycerol, PEG 200 coating on fresh cut apple cubes, chitosin coating on sliced mangoes etc.

Thus, the respiration rate is decreased(Makita et al., 1991; Wong et al., 1992), weight loss is reduced(E. Baldwin et al., 1999), and overall delayed senescence without loss of colour, gloss, sensory properties of fruits are the major effects that can be observed in coated fruits during storage due to application of edible coatings.

6. Conclusion

Edible films and coating technology is very promising and has given the desired results for enhancing the shelf life, quality and safety of perishable food products such as fresh and minimally processed fruits. Although considerable efforts have been dedicated to understand and modify film properties, it still remains to be a major challenge. Available coatings still lack the required sensory acceptance regarding their impact on taste, flavour and colour, which are of prime importance in food industry as it is based on consumer acceptance and feedback. Newer technologies which have shown promise at lab scale need to be commercially applied to give better results and improve consumer acceptance. Coatings should be designed to provide highly specific functional performances which are required by different food types to further enhance their performance.

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