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Scientific Information

Role of Biodegradable Edible Films and Coatings in Food Industry

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Abstract

Edible films and coatings are promising systems for the improvement of food quality, shelf life, safety and functionality. They can be used as individual packaging materials, food coating materials, active ingredient carriers, and to separate the compartments of heterogeneous ingredients within foods. The efficiency and functional properties of edible film and coating materials are highly dependent on the inherent characteristics of film-forming materials, namely biopolymers (such as proteins, carbohydrates, and lipids), plasticizers, and other additives. Edible films or coatings are generally defined as stand-alone thin layer of materials. They usually consist of polymers able to provide mechanical strength to the stand-alone thin structure. Films can form pouches, wraps, capsules, bags or casings through further fabrication process. Coatings are a particular form of films that are directly applied to the surface of food materials. Edible films and coatings are produced from edible biopolymers and food grade additives. Film forming biopolymers can be protein, polysaccharides (carbohydrates and gums) or lipids. Edible film and coating enhances the quality of food products, protecting them from physical, chemical and microbiological deterioration.

Keywords: Edible Films; Edible Coatings; Food Grade; Food Industry

Introduction

Edible films and coatings are promising systems for the improvement of food quality, shelf life, safety and functionality. They can be used as individual packaging materials, food coating materials, active ingredient carriers, and to separate the compartments of heterogeneous ingredients within foods. The efficiency and functional properties of edible film and coating materials are highly dependent on the inherent characteristics of film-forming materials, namely biopolymers (such as proteins, carbohydrates and lipids), plasticizers and other additives. Edible films or coatings are generally defined as stand-alone thin layer of materials. They usually consist of polymers able to provide mechanical strength to the stand-alone thin structure. Films can form pouches, wraps, capsules, bags or casings through further fabrication process. Coatings are a particular form of films that are directly applied to the surface of food materials. Edible films and coatings are produced from edible biopolymers and food grade additives. Film forming biopolymers can be protein, polysaccharides (carbohydrates and gums) or lipids. Edible film and coating enhances the quality of food products, protecting them from physical, chemical and microbiological deterioration.

Edible film and coating formation

- Whey protein-based edible films were produced by heating and irradiation.
- Protein cross linking facilitates to get a flexible, easy to handle film.
- Whey protein-based films involved heat denaturation at 75-100°C in aqueous solution,

Resulting in production of intermolecular disulfide bonds, which provide partial film structure (www.enwikipedia.org).

Heat treatment promotes water insolubility, which may be beneficial to maintain film and food integrity.

Plasticizers

- Plasticizers decrease activation energy for diffusion of gases and vapors through the film
- Plasticizers can decrease elasticity and cohesion.
- Plasticizers used in film systems are monosaccharides (glucose), disaccharides (sucrose), oligosaccharides, polyols (sorbitol, glycerol, mannitol, glycerol derivatives and polyethylene glycols) and certain lipids and derivatives (phospholipids, fatty acids, surfactants, etc.).
- Lipids or waxes may interfere with polymer chain to chain interaction causes reduction of film strength resulted in increased of film flexibility in whey proteins.
- Water acts as plasticizer for edible films and coatings, and hydrophilic plasticizers generally attract additional water.
- Glycerol and propylene glycol act as plasticizes showed secondary role, since they enhanced significantly the formation of cross-links within milk proteins (e.g. caseinates).
- Whey protein film need 10 percent to 60 percent plasticizers at on dry basis, depending on the rigidity of the polymer.
- It has been shown that hydrolyzed WPI has greater solubility and emulsifying activity, while allergenicity of WPI is reduced due to the hydrolysis process.
- Solubility of (hydrolyzed WPI edible films (30-75 per cent soluble protein) at 5 and 10 per cent degree of hydrolysis was found higher than that shown by unhydrolyzed WPI (about 3 per cent) under equal plasticizer (G) concentration.
- Insoluble films used on high moisture foods, while readily soluble films can find use in water soluble pouches.

Additives

- Edible films and coatings could have active agents, such as emulsifiers, antioxidants, antimicrobials, nutraceuticals, flavors and colorants.
- Food quality and safety enhanced up to the level where the additives interfere with physical and mechanical properties of the films.
- Emulsifiers are surface active agents of amphiphilic nature able to reduce the surface tension of the water-lipid interface or the water air surface.
- Emulsifiers are essential for the formation of protein or polysaccharide films containing lipid emulsion particles.
- Emulsifiers modify surface energy to control the adhesion and wet ability of the film surface.
- Antioxidants and antimicrobial agents can be incorporated into film-forming solutions to achieve active packaging or coating functions.
- They provide additional active functions to the edible film and coating system to protect food products from oxidation and microbial spoilage, resulting in quality improvement and safety enhancement.
- When nutraceutical and pharmaceutical substances are incorporated into edible films and coatings, the system can be used for drug delivery purposes.
- Flavors and colorants can be incorporated to improve the taste and the visual perception of quality, respectively.

Materials used for edible films and coatings

- The selection of materials for manufacturing edible film is based on its properties, to act as a barrier to moisture and gases and mechanical strength.
- Types of edible coating are categorized on the basis of base material used for preparation of edible coating.
- Various materials used for manufacture of edible coating are shown below

Classification

Edible films and coatings

Protein based	Polysaccharide based	Lipid based
Zein films and coatings	Seaweed extract	Whey-protein
Casein films and coatings	Chitosan	Emulsion film
Whey proteins films	Pectin	Zein-wax film
Soy protein films	Gums	
Collagen and gelatin	Cellulose	
Egg albumin	Sugar	

Table a

Protein based

- Proteins are the excellent starting materials for films and coatings.
- The distribution of charged, polar and non-polar amino acids along the protein chain creates chemical potential
- Proteins have multiple sites for chemical interaction as a function of their diverse amino acid functional groups, which can allow for property improvement and tailoring.
- Chemical changes can improve the stability of films and coatings.
- Cross-linked protein films are often more stable
- Protein-based films and coatings are biodegradable and compostable.
- During degradation they release the nitrogen, which had a fertilizer property which is not available with other non-protein-based films and coatings.
- The bioactive peptides produced upon digestion of proteins (dairy sources in particular) have antihypertensive and radical scavenging health benefits.

Composition

- Films and coatings may be made from proteins of both animal and plant origin.
- Protein-based films and coatings are prepared from solutions comprised of three main components: protein, plasticizer and solvent.
- The properties of the final film are affected by the intrinsic properties of the film or coating components and extrinsic processing factors.
- Intrinsic properties of proteins include amino acid composition, crystallinity (of the protein and/or plasticizer), hydrophobicity/hydrophilicity, surface charge, pI, molecular size, and three-dimensional shape.
- The presence of cysteine allows for potential disulfide bridge formation, as noted for beta-lactoglobulin.
- High concentrations of leucine, alanine and other nonpolar amino acids can create hydrophobic proteins.
- Extrinsic factors include processing temperature, drying conditions, pH, ionic strength, salt-type, relative humidity during processing and storage, shear and pressure.

Whey protein

- Whey is a by-product of the cheese-making process
- Whey proteins are technically defined as those that remain in the milk serum after coagulation of the caseins at a pH of 4.6 and a temperature of 20°C.
- Whey protein is comprised of beta-lactoglobulin, alpha-lactalbumin, bovine serum albumin and immunoglobins.
- Whey proteins had evenly distributed net negative charge over the protein chain.
- Casein had unevenly distributed net negative charge over the protein chain.
- The hydrophobic, polar and charged amino acids are also uniformly distributed.
- Consequently, the proteins fold so that most of the hydrophobic groups are buried within the whey protein molecule.
- The protein interactions between chains determine film network formation and properties.

Collagen

- Collagen is a fibrous, stromal protein extracted from connective tissue, tendons, skin, bones and vascular system which are waste products of meat processing.
- Collagen is made from three parallel alpha-chains, which combine to make a triple stranded super helical structure.
- The amino acid sequence of collagen is dominated by a repeating trio of Gly-X-Y residues.

Gelatin

- Gelatin is formed when collagen is exposed to a mild heat treatment under acidic or alkaline conditions.
- Collagen is partially denatured, but upon cooling, partially reforms the triple helix structure.
- The resulting protein material is called as gelatin.
- Gelatin contains a large amount of proline, hydroxyproline, lysine and hydroxylysine.

- Gelatin has good gelling properties so used in the food industry to thicken and texturize foods.
- Gelatin has excellent foaming properties helping to form a good edible film former.
- Gelatin has been used as a coating by the food and pharmaceutical industry for years.

Eggalbumen

- Egg albumen is the second major component of liquid egg white after water contain
- Egg albumen makes up approximately 10% of the total liquid egg white weight.
- Egg albumen has five main protein fractions: ovalbumin, ovotransferrin, ovomucoid, ovomucin and lysozyme.
- During heat denaturation, egg white proteins form stable intermolecular beta-sheet structures.
- Between ovalbumin, ovotransferrin and lysozyme.
- Above 60°C, egg white proteins unfold, exposing their internal sulfhydryl groups that can affect disulfide bond formation and surface hydrophobicity increases.

Soyprotein

- Soy protein is comprised of a mixture of globular proteins.
- Approximately 90% of soy proteins separate into either a 2S, 7S, 11S or 15S fraction, based on molecular weight and sedimentation coefficient.
- The two main globular proteins are beta-conglycinin (7S globulin) and glycinin (11S globulin), which make up 37% and 31% of the soy proteins, respectively.
- Conglycinin (140–170 kDa) consists of various combinations of three subunits, which are heavily glycosylated.
- As with other film forming proteins, glycinin is known to be a gelling agent, emulsifier and foaming agent.
- Heat and alkaline conditions can denature soy proteins, affecting film formation.
- Similar to beta-lactoglobulin (whey protein), glycinin (11S protein) forms intermolecular disulfide bonds when denatured, which bonds affect the tensile properties of a formed film.
- Soy protein association and stability is dependent on the pH and ionic strength.

Cornzein

- Zein protein from corn has some unique characteristics compared to most other agricultural proteins used for edible films and coatings.
- Zein possesses a high percentage of nonpolar amino acids and low proportions of basic and acidic amino acids.
- The three primary amino acids in corn zein protein are glutamine (21–26%), leucine (20%) and proline (10%).
- Consequently, corn zein protein is insoluble in water, a characteristic that affects the barrier properties of its films.
- The two major fractions of zein are alpha-zein and beta-zein.
- Alpha-zein is soluble in 95% ethanol, and makes up approximately 80% of the total prolamines present in corn, while beta-zein is soluble in 60% ethanol.
- A helical secondary structure dominates zein proteins.
- When formed into films, zein is glossy, tough and greaseproof, with a low water vapor permeability compared to most other agriculturally-based protein films.
- Zein has been commercially used as a coating for medical tablets and has the potential to be used in biodegradable packaging.

Function and applications of protein-based films

- Based on the required tensile, barrier and appearance characteristics and properties, protein-based edible films for specific applications can be designed.
- At the current state of edible film technology, the best application potential lies in protective coatings for foods.
- When applied to the surfaces of foods as a coating, protein-based edible films can protect food from chemical or microbial damage, thus lengthening product shelf life and maintaining high product quality.
- Most protein-based films provide excellent barriers to oxygen.
- This characteristic has been utilized to effectively protect high-fat foods, which are known to form rancid off-flavors, due to oxidation.

- As barriers to mass transfer of carbon dioxide, protein-based coatings have been found to increase the shelf life of eggs and fresh-cut fruits.
- Egg quality drops over time as carbon dioxide migrates out of the shell, causing changes to the internal pH.
- These pH changes can deleteriously affect color and yolk quality.
- The shelf life of whey protein-coated Grade A eggs could be extended one week longer than uncoated eggs, when stored under ambient laboratory conditions.
- In the case of fresh-cut produce, browning and ripening times are major factors determining product shelf life.
- Protein-based edible coatings that have moderate oxygen, carbon dioxide and water vapor permeability can be applied to the surfaces of fresh-cut produce to extend product shelf life by delaying ripening, inhibiting enzymatic browning, reducing water loss and minimizing aroma loss.
- Whey protein coatings significantly delayed browning in fresh-cut Macintosh apples and Russet potatoes.
- Edible films used to protect fresh-cut produce have advantages over modified atmosphere packaging or treating the cut surfaces with ascorbic acid (which inhibits browning).

Polysaccharide and gum-based edible films and coatings

Polysaccharide gums are hydrocolloids of considerable molecular weight and are water-soluble.

They dissolve in and form intensive hydrogen bonds with water.

Because of the size and configuration of their molecules, these polysaccharides have the ability to thicken and/or gel aqueous solutions as a result of both hydrogen bonding between polymer chains and intermolecular friction when subjected to shear are hydrocolloids of considerable molecular weight and are water-soluble.

They dissolve in and form intensive hydrogen bonds with water.

Most abundant natural polysaccharides.

Starch films are often transparent, translucent, odorless, tasteless and colorless.

Packaging and coating of food products, because of their edibility and low permeability to oxygen.

Edible starch films are the most effective forms of soluble packaging in terms of

- Performance
- Adaptability to products
- Production operations
- Costs

Roots and tubers are very good source of easily recoverable starch.

Starch and gum improve the tensile strength and both water vapor and oxygen permeability.

Bioplastics (edible film) to reduce

- The environmental impact.
- Disposal costs.

Hydrodegradable films

- Corn (maize), potatoes or wheat.
- Biodegradable film meets the ASTM standard.
- Degrades at least 90% within 180 days or less under specified conditions.

Isolation of starch

- Starches were isolated from potato, sweet potato and taro.
- Tubers were washed, peeled and shredded.
- Shreds were put into plain water (pH 6.8).
- After that the shreds were put in water solution which contains chemicals, such as potassium metabisulphite (KMS) (0.25%) in combination with citric acid (0.12%) to improve the color of starch.
- Then shreds were ground with high speed blender to a fine paste.
- The water in 1:2 ratios was added to paste, which then sieved through 80µ sieve.
- The filtered part was allowed to precipitate.

- Dried in an oven at 50°C to a moisture content of 10% (wet basis).
- After drying starch was grounded in high speed grinder and then passed through 100μm sieve and stored in air tight containers at ambient temperature.

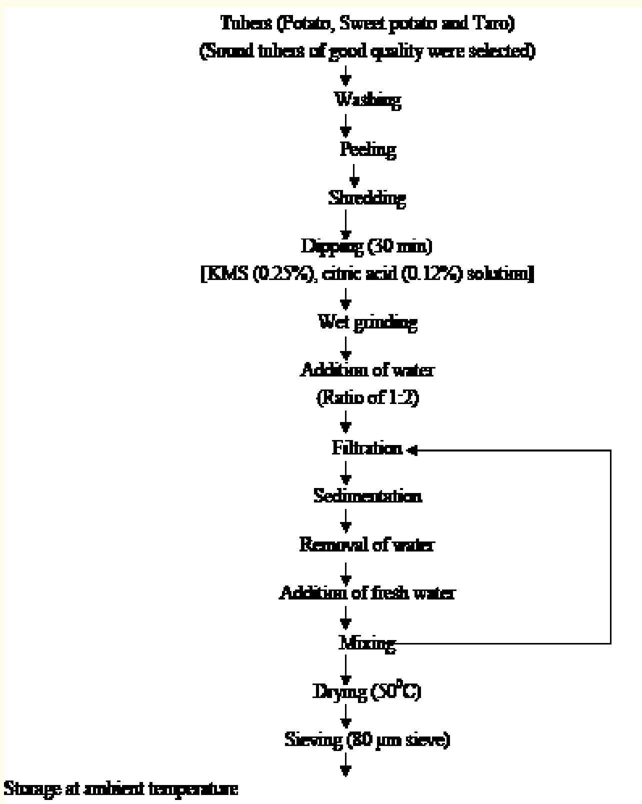

Figure a

Flow chart for the isolation of tuber starch

Preparation of starch films

- Film-forming solution containing 3% to 5% of native and modified starches.
- Glycerol at concentrations of (0.25g/g on dry starch basis) was used as plasticizer.
- Heated to boiling temperature on hot plate with constant stirring for 10minutes by magnetic stirrer.
- Mixture was cooled till bubbles vanish and poured (hot) onto the plastic trays.
- The trays containing the film forming solution were then dried in a cabinet drier at 50°C for 5hr.
- The dried films were peeled off from the trays.

Structures in starch films

- Semi crystalline, containing both amorphous and crystalline phases.
- Freshly prepared starch films are basically amorphous.
- Aged starch films are semi crystalline, the majority (>70%) is still amorphous.
- Starch films normally show a B-type XRD pattern.

Crystalline structure

- **A-type** - Drying temperature is between 80°C and 100°C.
- **B-type -** Drying temperature is not higher than 60°C at ambient relative humidity.
- **C-type -** Drying temperature is between 60 and 80°C.

Degree of crystallnity of starch films depends upon

- Air humidity
- Temperature during storage
- The content of the plasticizer

Water sorption

- Both the glass transition temperature and the degree of crystallinity.
- Water sorption isotherms are commonly used to study the effect of temperature and relative humidity on the water content of starch films.
- Starch films possess higher water sorption than native starches because the latter have a compact granular structure.

Mechanical properties depend on

- The degree of crystallinity.
- Crystallites: tend to strengthen and stiffen the films.

- Amylose films exhibit improved mechanical properties over amylopectin films.
- Storage can affect the mechanical properties.
- Increasing amylose content leads to improved mechanical properties including tensile strength and elongation.
- Plasticizer contents vary over a wide range (15-60%).
- An anti-plasticization effect found when the plasticizer content is low.
- Glycerol - 15%.
- Sorbitol - 27%

Classification

Sources

- **Natural:** Based on renewable resources such as starch and cellulose (e.g. seaweed, corn and wheat straw)
- **Synthetic:** Based on petroleum products.

Compostable

- Synthetic, non-biodegradable polymers
- Synthetic, biodegradable polymers
- Natural, non-biodegradable polymers
- Natural, biodegradable polymers.

PLA

- PLA produced by Cargill Dow uses corn starch as a feedstock
- Milling of corn
- Fermentation - Dextrose to lactic acid
- Condensation - cyclic lactide molecule
- Lactide is purified through vacuum distillation
- The polymer is produced in loose-fill pellets from the plant
- After its useful life PLA can be disposed off, composted or recycled

Limitations

- Starch is very reactive with water.
- The maximum useful temperature is 114°F.

Cargill dow process

Figure b

Poly hydroxy alkanoates

- The existence of PHAs since 1925 in bacterial cells.
- There are two different ways to synthesize PHAs.

Processing by fermentation

1. Growing the plant source such as corn
2. Harvesting the plant source
3. Transporting the plants
4. Extracting the glucose from the plant
5. Fermentation of the glucose into cells containing PHA using microorganisms
6. Washing and spinning the cells twice to release the PHA in the cells
7. Finally concentrating and drying the PHA into a powder form

Processing by growth of PHA in plant cells

1. Growing the plant source such as corn
2. Harvesting the plant source
3. Transporting the plants
4. Washing and spinning the cells twice to release the PHA in the cells
5. Finally concentrating and drying the PHA into a powder form.

Advantages

1. Fully compostable
2. Biodegradable in many environments (water or soil).
3. Compost under aerobic and anaerobic conditions and when exposed to natural organisms

Thermoplastic starches

- Made from starches such as corn, potatoes and wheat
- TPS polymers do not have to be fermented
- Contain between 10 and 90% starch but must have at least 60% starch

Polyvinyl alcohol

- Water soluble polymer prepared by hydrolysis of polyvinyl acetate
- Not used as food packaging
- Agricultural chemicals, dyes and pigments, as well as water-soluble laundry bags for hospitals and detergent pouches
- TPS shows a very low permeability for oxygen
- Permeability of TPS for water vapour is very high

Drawbacks

- More sensitive to humidity
- Quick ageing due to water evaporation

Overcome by

- Blending the thermoplastic starch with hydrophobic synthetic polymers
- Production of more hydrophobic TPS derivatives (starch ester)

Main players in biodegradable polymers and their trade names

Figure c

Films from Non-starch poly Saccharide

Cellulose

- Starting material for edible coatings
- Reduce moisture loss and reduce the amount of oil absorbed by fried foods
- Used to delay ripening in climatic fruits like mangoes, papayas and bananas
- Reduce enzymatic browning in sliced mushrooms
- CMC, MC, HPC, and HPMC, have been applied to a variety of foods to provide moisture, oxygen or oil barriers, and to improve batter adhesion
- MC films provide an excellent barrier against migration of fats and oils

Chitosan: Derived from chitin

Uses

1. Flocculent
2. Clarifier
3. Thickener
4. Gas-selective membrane
5. Promoter of plant disease resistance
6. Wound-healing factor agent
7. Antimicrobial agent

Alginate

1. Derived from brown seaweed known as **Phaeophyceae**
    - M block (p-D-mannuronic acid)
    - G block (poly a-L-guluronic acid)
    - MG block (containing both polyuronic acids)
2. Alginate based films are impervious to oils and fats
3. Coatings are good oxygen barriers
4. Reduces weight loss as well as the natural microflora counts in minimally processed carrots, stored lamb carcasses fish and shrimps.

Carrageenan

Derived from red seaweed.

- Kappa (K)
- Iota (L)
- Lambda **(A).**

Contain the lowest number of sulfate groups.

Applications

- Applied for a long time to a variety of foods to carry antimicrobials or antioxidants and to reduce moisture loss, oxidation, or disintegration.
- Coating applied on cut grape fruit.

Agar

- Derived from a variety of red seaweeds like carrageenan.
- Antibiotics, bacteriocins or natural antimicrobial compounds can be incorporated in agar-based films.
- To improve shelf life and to control pathogenic bacterial growth.
- Reduction in Salmonella typhimurium population of 1.8 to 4.6 log cycles after 96 hours of storage at 4°C.

Pectin

- High-methoxy pectin forms excellent films.
- Blends of pectin and starch can be used to make strong, self-supporting films.
- Making biodegradable drinking straws.
- Plasticized blends of citrus pectin give strong, flexible films, which are thermally stable up to 180°C.

Microbial polysaccharides

- Pullulan, levan, and elsinan.
- Clear, odorless and tasteless, and have good oxygen barriers.
- Oxygen barriers to prolong food shelf life.
- Pullulan - Biodegradable packaging films.
- Levan and elsinan - edible coating materials for foods and pharmaceuticals.

Figure d

Advantages

1. Edible and biodegradable film.
2. Reduces environmental pollution.
3. Enhance the organoleptic properties of packaged food by incorporating flavorings, colorings and sweeteners.
4. Supplement the nutritional values of the food.
5. Individual packaging of small of foods.
6. Carry antimicrobial and antioxidant agents.
7. Microencapsulation of food flavorings and leavening agents to efficiently control the release rate into interior of foods.
8. Used in multi layer food packaging materials together with non- biodegradable films
9. Coatings can be milky or clear

Some commercial edible coatings

- Nutre-Seal: contains modified cellulose polymers
- Nutri-Save: contains carboxymethyl chitosan
- Pro-long is based on sucrose polyesters of fatty acids and sodium salts of carboxy-methyl cellulose
- Sealgum and Spraygum are based on gum acacia and gelatin.
- Shellac is a resin secreted by an insect

Future of edible coatings

- Great potential, but limited application.
- Mainly used to control moisture loss and respiration.
- Used to alter surface appearance.
- Could be used as a carrier for additives.
- Main applications are with dry nuts, dried fruits (e.g., raisins) and freeze dried foods.

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