Functionality of protein-Based edible coating - review

Hauzoukim, Sagarika Swain, Biswajit Mohanty

Abstract
Consumer demand for convenience package and consumption, safe microbiologically, longer product shelf-life and effect of packaging material on environment is forcing food processor and researcher to develop new technique in food processing, cooking, handling, and packaging strategies. Most of ready-to-eat foods are exposed to post-process contamination, leading to spoilage and reduced shelf-life. Biopolymers extracted from biomass, synthesized from bio-derived monomers or produced directly by microorganisms with the advantages of biodegradability, process ability, no pollution to food, abundant and renewable have become the leading food packaging materials. Furthermore, the raw materials to produce biopolymers are low-cost, some coming even from by-product of agriculture and fish processing waste. Proteins-based edible films can be incorporated into foods to impart nutritive value and functional properties. The materials to develop protein-based coatings and packaging films can be divided into two classes: plant proteins and animal proteins. Proteins referred in this review are broadly classified under cereal, milk, oilseeds, collagen and gelatin based. Proteins-based edible coating has excellent gas barrier properties and good mechanical properties. However, the hydrophilicity nature of proteins makes the protein-based films poor water barrier properties. The application of plasticizers and treatments can improve the protein-based films and coatings. The addition of physical and chemical active compounds into protein-based films can increase the functional properties which can inhibit or delay the growth of microorganisms and the oxidation of lipids thereby increase its shelf-life. The review summarized the advances and research about the functional properties protein-based films and coatings in food packaging with examples.

Keywords: Protein-based films and coatings; functionality; plasticizers; applications in food

Introduction
Consumers demand for high quality foods with enhanced keeping quality of raw and Ready-to-Eat foods with minimal changes in nutritional and sensory properties. Food processor and researcher are exploring an alternative or novel processing technologies to provide safe, fresher-tasting, nutritive foods without undesirable changes in food due to processing [5, 6]. Use of edible coatings to preserve food is not a new concept but have gain interest in recent times due to their protective functions. It will minimize the concern over disposal of packaging materials; reduce utilization of synthetic material [9, 4] and use of under-utilized agriculture products for edible film forming [5, 6, 7, 8]. The choice of packaging material will varies according to the specific food and major contributing factor for quality deterioration [9, 4]. The edible coatings can simplify the total packaging structure [9, 3].

Background of Edible coating
An edible film can be defined as a thin layer used to coat food or act as a barrier between the food and the environment [10]. The first free-standing edible film “Yuba” was developed during the 15th century in Japan from soymilk and was used for food preservation [11, 12]. Edible films can be prepared from proteins, polysaccharides, and lipids. Edible coatings derived from proteins, lipids and polysaccharides have solute, gas, and vapor barriers functioning properties. During the 12th century, the Chinese applied waxes on oranges and lemons to retard water loss [13, 14, 15]. Coating of foods with fat also known as ‘larding’ was used in England in 16th century to test their moisture barrier property [16]. Since the 1930s, hot melted paraffin waxes use to coat citrus fruits in the United States, and carnauba wax and oil-in-water emulsions to coat fresh fruits and vegetables since the 1950s [17, 18, 19]. [20] Reported that edible films can extend shelf life of fresh fruits by delaying moisture loss. Edible coatings have wide application as casing for sausages and chocolate coatings for nuts and fruits which
do not require to be removed before consumption. Edible films mechanically protect foods by preventing the contamination from microorganisms; prevent quality loss due to mass transfer (e.g., gases, moisture, flavours, etc.). Edible films become a vehicle for incorporating natural or chemical antioxidants, antimicrobial agents, enzymes, other functional ingredients such as minerals, probiotics and vitamins [21, 9]. This review will discuss the rationale use of protein base edible coatings on fruits, vegetables, meats, poultry, and sea foods and summarizes research findings on the effectiveness of and the problems associated with various types of coatings.

**Film-forming techniques**

Different techniques are used for film forming depends on the different material or substances used. Some of which require solvent extraction, thermal gelation, and solidification of melt have been developed for forming edible films.

A. Hydrocolloid edible films are produced solvent extraction, a continuous structure is produced. The physical and chemical interactions between molecules help to stabilize the product. Solvents used are water, ethanol, or acetic acid which contains additives such as plasticizers, cross-linking agents, solutes, etc.

B. In protein films the solution is heated denaturation, gelification, or precipitation followed by rapid cooling produce gelation and coagulation [22].

C. Lipid based films are melted and solidified [23].

Plasticizers added with biopolymers are used for protein based edible films to modify and increase its functionality of the edible films. Plasticizers inclusion will decrease protein interactions while increasing both the polymer chain mobility and intermolecular spacing [24]. The biopolymers added help in film-forming mechanisms by intermolecular forces such as covalent bonds (disulfide bonds) cross linking, hydrophobic, electrostatic, or ionic interactions. One important factor in the film forming mechanism is to control the fabrication process conditions, should be suitable for food process (pH modification, salt addition, use food grade solvent, drying, enzyme modification, heating or reaction with other chemicals). If not controlled, alteration of the kinetics and reaction mechanisms may occur [25, 26]. The type and concentration of plasticizer influences the properties of protein films [27, 28]. Film additives are mostly small molecules having low molecular weight and high boiling point compatible with the polymers [29]. Plasticizers increase extensibility and decrease the brittleness of the film which is an important characteristic of the packaging applications. Some of the food grade plasticizers are sucrose, sorbitol, mannitol, glycerol, polyethylene glycol etc. Water also improves protein films [30] but film properties are affected by moisture. Common covalent cross-linking agents such as glutaraldehyde, calcium chloride, tannic acid, and lactic acid are used to improve water resistance, cohesiveness, rigidity, mechanical strength, and barrier properties [31, 32, 33].

The benefits of using Edible Coatings on foods (Vegetables, Fruits, Meat, Poultry and Seafood)

Edible coatings are use for their functional properties in order to meet challenges related with nutritious, stable, and high quality foods for a better economic and marketing safe. Some of the benefits are discussed below

1. Edible films and coatings enhance the quality of food products, protecting them from physical, chemical, and biological deterioration [34]. It can improve the physical strength of the food products, reduce particle aggregation, and improve appearance [35, 36].

2. Prevention of moisture loss during storage of fresh or frozen foods as edible coatings have a good moisture barrier properties which prevent weight loss due to moisture evaporation. In other case application of edible coatings can prevent formation of juices on the package when fresh meat, poultry, fish cuts are packaged in retail plastic trays, which are unattractive to the consumers. While preserving the food, the production cost could also be reduced as no extra moisture absorbent is required. [34, 37, 38, 3, 39].

3. Use of edible coatings of low oxygen permeability helps to reduce the rate of rancidity and brown discoloration in meats but creating an anaerobic conditions should be avoided [34, 38].

4. Pre-heated edible coating solutions just before application could reduce the amount of spoilage and pathogenic microorganisms and partially inactivate deteriorative proteolytic enzymes at the surface of coated foods [34].

5. Edible coatings could prevent loss of colour, volatile flavour and prevent pick-up of foreign odour in foods [37, 38, 3, 39].

6. When edible coatings added with antioxidants or antimicrobials helps to delaying meat rancidity and discoloration, and reducing microbial loads [37, 38, 3, 39].

7. Edible coatings when applied on the surface of food before battering in a battered and breaded product reduce oil uptake during frying and loss of moisture thereby improving the products’ nutritional value [40].

8. The greatest benefits of edible film and coating materials are their biodegradable and edibility nature [30, 3].

9. Carrier of bioactive compounds- Enrobing acts as a carrier for various synthetic or natural antimicrobial and antioxidant substances [41, 42, 43, 44, 45]. Reported that when added butylated hydroxytoluene and butylated hydroxyanisole in enrobed pork patties, it help to extend shelf life of enrobed pork patties.

**Classification of edible films:**

Edible films mainly classified under three major categories viz. proteins, polysaccharides, and lipids.

1. Proteins based- wheat, gluten, collagen, corn zein, soy, casein, and whey protein [34].

2. Polysaccharide based - Alginate, dextrin, pectin, and cellulose derivatives [34].

3. Lipids-waxes, acylglycerols, and fatty acids (Debeaufort and Voilley, 1995; Park et al., 1995) [46, 47].

4. Composite films – made by combining both lipid and hydrocolloid components [29].

**Proteins based edible coating**

Edible films from animal and plant proteins, such as wheat, gluten, collagen, corn zein, soy, casein, and whey protein and their properties and formation was of recent interest due to their numerous functional properties [48, 34]. Functional properties can be defined as “those physical and chemical properties that influence the behaviour of proteins in food systems during processing, storage, cooking and consumption” [49, 50]. It stated that “the physico-chemical properties that influence functional behaviour of proteins in food include their size, shape, amino acid composition and
sequence, net charge, charge distribution, hydrophobicity, hydrophilicity, structures (secondary, tertiary and quaternary), molecular flexibility/ rigidity in response to external environment (pH, temperature, salt concentration), or interaction with other food constituents" [51]. Reported that edible protein coatings provided a method of extending postharvest storage of fruits and vegetables. Protein films are hydrophilic in nature possessing poor water vapor barrier property [53], but exhibit better oxygen, carbon dioxide barrier properties and mechanical properties than polysaccharide films [24]. The poor water vapour permeability can also be improved by the incorporation of hydrophobic materials such as lipids [53] but the incorporation of lipid materials could adversely affect the sensory characteristics of films. WPI and mesquite gum (MG) are showed compatible when incorporated with antimicrobial agents [59]. The high water vapour transmission rate can also be overcome by the addition of plasticizers. Some protein are insoluble in water but are dissolve using a plasticizer or solvents whereas the proteins soluble in water produce coatings of varying solubility depending on the protein type and source and the conditions of treatment and coating formation. The concentration, composition, size, and shape of plasticizers all affect the properties of protein films [55, 56, 57, 58, 59, 60]. Studied about the good oxygen barrier properties in low relative humidity environments of edible films from collagen, wheat gluten, corn zein, soy protein, and whey protein. While coating raw meat, poultry or seafood, the protein-based edible coatings are susceptibility to proteolytic enzymes present in the foods. Labelling of the food coated with protein based is important due to some individuals allergic to protein fractions of milk, egg white, peanuts, soybeans etc. or other adverse effect to the individuals. Some individuals are gluten intolerance due its gliadin fraction in particular, known as celiac disease or gluten-sensitive enteropathy or non-tropical sprue [48]. Some individuals show lactose intolerance due to deficient in lactase [61].

1. Cereal Protein

Film formation from corn zein, the prolamin fraction of corn proteins, and from wheat gluten, a mixture of the prolamin and glutenin fractions of wheat proteins, has been studied extensively [57]. Gluten films have good oxygen isolation performance with resistance to water vapor and mechanical properties [3]. Addition of nonpolar hydrophobic substance like mineral oil in the film can reduce 25% of water vapor permeability when compared to the control group [62]. Thermal treatment can improve the mechanical properties of the gluten-based films for the casting films that were obtained through covalent crosslinking of gliadin polypeptide [63, 64]. Wheat gluten on eggshells improved shell strength, reduced microbial contamination [65]. Recent studies have evaluated properties of films from sorghum kafirin and rice bran protein [66]. A composite of gluten and SPI (soy protein isolate) can reduce fat deterioration in peanuts [67]. Zein is a by-product during corn processing constitute about 45–50% of corn proteins [68, 69]. Mentioned that corn zein has been used in commercial coating formulations for shelled nuts, candy, and pharmaceutical tablets. The use of corn zein as an edible coating or packaging film for cooked meat and poultry has recently been suggested. Tomatoes coated with corn-zein (CZ) protein film delayed in ripening without adverse effects. Tomatoes delayed color development, loss of firmness, and weight loss [70]. Corn zein when coated on precooked pork chops reduce lipid oxidation (significantly lower thiobarbitouric acid values) but have poor moisture barrier properties after storage at 4°C for 6 and 9 days [71]. Precooked beef patties coated with wheat gluten reduce the moisture loss during a refrigerated storage [72]. Corn-zein applied to apples and pears, shows different in the respiration rate where the respiration rate of the former is decreased, but the opposite in pear. However, the weight losses of both the fruits are delayed [47]. Zein coating incorporating with polymeric chelator extends fish ball shelf life at refrigerated condition, 4°C to 19 days [73].

2. Milk protein

Whey is a by-product during cheese manufacturing, rich in cysteine, methionine and sulfur-containing amino acids. Whey-based films prepared from whey protein concentrates (WPC) and isolates (WPI) have a protein content of 90% and 50–80% respectively [74]. The film forming ability of whey based film depends on the thermal denaturation of whey protein in an aqueous solution. The three-dimensional structure of whey protein is modified by heating which exposed the internal hydrophobic and SH groups having the hydrophobic and intermolecular S–S bonding interactions promoted upon drying [75, 76]. When the pH of film-forming solution in WPC is adjusted to 6.6 and heating temperature to 75°C, an uniform film was obtained [77]. Ultraviolet (UV) radiation and ultrasounds (US) can also improve the properties of the whey-based films. The whey-based films made with plasticizers are flexible. Whey proteins have poor moisture barrier due to hydrophilic nature but produces films flexible, transparent, and flavourless when a plasticizer is added [78, 79]. Lipid materials like fats and oils could increase the hydrophobicity of whey-based films and improve the poor moisture barriers properties. The lipid materials can be from plant oils [80, 81, 82, 83, 84, 85], fatty acids [86] and acetylated monoglycerides [87]. Treatment with UV radiation and alkali for e.g., 7 or 9 to the WPC film-forming solutions, the film become strong, puncture resistance of the films is improved. Studies of whey protein based coatings on common breakfast like raisins, cereals, cheese pieces and frozen peas, and on peanuts for its oxygen barriers properties. Whey protein or whey protein with carbohydrate was used to microencapsulate food additives [71]. Edible coating prepared from whey protein isolate with ascorbic acid and citric acid as an antioxidant were spray on King salmon, the edible coating does not have affect moisture loss rate but shows a delayed on the onset of lipid oxidation and reduced peroxide values in frozen [88, 89]. Reports frozen King salmon coated with whey protein powder shows 42–65% reduced in moisture loss and a delayed in lipid oxidation. Whey protein with acetylated monoglycerides on nuts show delayed in rancidity [80, 91, 92]. Whey protein, whey protein isolate (WPI), wheat gluten (WG) on eggshells improved the shell strength, greater puncture strength and reduced microbial contamination than those of non-coated eggs [65]. Addition of sodium dodecyl sulfate (SDS) to soy protein isolate increase the extendibility of the films substantially while simultaneously improved the moisture barrier properties [93, 94]. The addition of cysteine increases the film tensile strength. Irradiation and heat curing after the film formation improve the soy protein films performance due to the bityrosine formed between two protein chains through irradiation which increase its mechanical properties. Heat curing increase the tensile strength from 8.2 to 14.7 MPa but the film elongation...
decreased from 30% to 6% \cite{95}. Thermal treatment with irradiation improves the mechanical properties of soy protein films \cite{96}. Precooked beef patties coated with soy protein reduced moisture loss compared to unpackaged patties after 3 days of refrigerated storage. “Fiji” and “Golden 95 delicious” variety of apples coated with soy protein improves the quality by delayed the changes in firmness, colour, and acidity \cite{97}. Lactoperoxidase system (LPOS)-Whey protein treated on rainbow trout fillet shows antimicrobial activities by reducing total specific spoilage organisms (Shewanella putrefaciens and Pseudomonas fluorescens) and extended the shelf-life from 12 days to 16 days on refrigerated storage \cite{98}. \cite{99} Reported that the use of ultrasound-treated whey protein coatings on frozen Atlantic salmon delayed lipid oxidation. Casein contains four main subunits: kappa-casein, beta-casein, alpha s1-casein and alpha s2-casein that make up 13%, 36%, 38% and 10% of the casein composition respectively \cite{100, 101}. Without further processing, casein can form films easily from aqueous solutions because of the strong inter-chain cohesion caused by their random-coil nature and a great number of formed intermolecular hydrogen, hydrophobic and electrostatic bonds \cite{102}. Caseins are easily water soluble, good emulsification properties, high nutritional value and easily availability makes caseins desirable biomaterials for the preparation of edible films \cite{103, 104, 105, 106, 107}. Caseins are more insoluble as compare to other protein which makes caseinate (mainly sodium caseinate) an alternative to traditional packaging materials. Although casein has many advantages there are defects that need to be improved. The interactive forces between non-polar and polar amino acid in the structure of casein causes shrinkage during the drying process and then become brittle which can be overcome by the addition of plasticizers like sorbitol or glycerol \cite{108}. The mechanical properties and elasticity can be improved by the modification of the polymer network through physical and chemical treatments can make the films functionality be improved \cite{104, 109}. Some of the agents applied to improve the quality are transglutaminase \cite{110, 111}, glutaraldehyde \cite{112}, genipin \cite{113, 114, 115}, tannic acid \cite{116} and wax \cite{115} are used as crosslinkers or by combination with polysaccharides \cite{116, 117} or lipid \cite{108, 109, 110}, pH alteration \cite{120}, photo-induced polymerization \cite{121}, pulsed light \cite{122}, Lactic acid–treated casein with sorbic acid is tested on papaya cubes inoculated with Staphylococcus rouxii, Aspergillus. niger. After 30days of storage 30% of the sorbic acid was retained and there is no growth of both the test organisms. A complete diffusion of sorbic acid is sorbic acid is observed within 24 hrs if not treated with casein. This shows that the edible film matrix helps to entrap the antimicrobial properties and reduced the diffusion during storage studies \cite{123}. Casein when applied to peeled carrots helps reduced dehydration and white blush formation \cite{124, 125} and when casein with acetylated monoglycerides used to coat celery sticks reduced dehydration \cite{126}. Sodium caseinate film reduced oxygen and carbon dioxide permeation when treating green bell peppers \cite{97}.

3. Oilseed proteins

Importance of protein structure in relation to the functional properties was reported by \cite{127, 128} study the functionality of proteinic products by modification of protein. The amount of water and proteins interaction is related with its amino acids profile and increases with the number of charged residues \cite{129}. Protein content from dehulled oilseeds ranges from 35% and 60% on dry weight basis. The antinutritional factors (phytic acid, trypsin inhibitors and tannins) and low protein solubility present in meals could limit its application. The application of aqueous processing, with or without enzymes hydrolysing the structural polysaccharides of the cell wall to enhance the extraction of oil will also improve the nutritional and functional properties of the protein \cite{130, 131, 132, 133}. Egg albumen and soy protein isolate mixture was use to stabilized dehydrated meat as describe by (Khan et al., 1993). Meat flavour was retained when soy protein as microencapsulating medium was use as coating while the product had good texture and rehydration characteristics (Torres, 1994).

4. Collagen

Unilever developed a more advanced technology where the collagen casing is co-extruded around the sausage meat batter \cite{132}. It is continuous and better controlled compared to conventional batch process where meat batter is stuffed into pre-formed casings. Furthermore, use of proteins other than collagen, such as wheat gluten, corn zein, soy protein, peanut protein, and feather keratin, in manufacturing of sausage casings has been suggested \cite{134}. Jones and Whitmore mixed ground collagen with aqueous mixture of lactic acid and glyceraldehydes setting pH 7, heated at about 75°C and coat on hamburgers which can withstand a cooking temperature. Collagen casings for sausage prepared from the regenerated corium layer of food-grade beef hides \cite{135}. An edible collagen film “Coffi” can reduce cook shrink, increase product juiciness, when coated on boneless hams, fish fillets, roast beef, and meat pastes \cite{135}. Beef steaks wrapped in Coffi collagen film both refrigerated and frozen/thawed exhibited significantly less fluid exudate than unwrapped controls. The thiobarbituric acid, color analysis and sensory results shows the collagen films had no significant effect on meat oxidation and color \cite{59}. Collagen used as casings for sausages, as studied by \cite{122}.

5. Gelatin

Gelatin is protein based polymer obtained from animal skin, bones, connective tissue and fish skin after partial hydrolysis of collagen. In the hydrolysis process, the raw animal material is treated with dilute acid or alkali and results in partial cleavage of the cross-links where the structure is broken down to “warm-water-soluble collagen”, i.e. gelatin \cite{136}. Preservations of meat and other food using coating of gelatin films were proposed by \cite{137, 138}. Gelatin is mainly use for microencapsulation of ingredients and coatings for tablet and capsule \cite{48}. Gelatin is readily soluble in water at temperatures above 40°C, which destroys the triple helical structure of collagen forming a viscous solution of random-coiled linear polypeptide chains. At about 20°C, gelatin formed a collagen like helices but short including only part of the material which forms a gel. Higher amino acid content in mammalian gelatin gives the advantage of better physical properties and thermostability than fish gelatin. Its film forming ability directly relates to its molecular weight. Molecular weight distribution and amino acid composition of gelatin defines its physical properties i.e., the higher the average molecular weight, the better the quality of the film. The quality of the gelatin film depends mainly on the degree of collagen cross-linking and the extraction procedure \cite{139, 70}, reported that when sprayed turkey steaks with an aqueous gelatin suspension with various antioxidants results in less lipid oxidation (lower peroxide values by 60–
90%) in the skin and meat fat compared with uncoated controls during frozen storage at −12°C for 6 months. This shows gelatin have shown potential as carriers of antioxidants, [140, 141] reported that gelatin from marine sources (warm- and cold-water fish skins, bones, and fins) can be alternative to bovine gelatin as it is free of the risk of outbreaks of Bovine Spongiform Encephalopathy and also religious sentiments [185]. Fish gelatin gives a better utilization as by-product of the fish-processing industry waste and providing a valuable source of gelatin [163]. The collagen content in the fish skin waste of Japanese sea-bass, chub mackerel, bullhead shark were found to be 51.4%, 49.8% and 50.1% (dry basis) respectively as reported by [144, 145]. Reported that Alaska pollock gelatin can be used up to 10 g/kg without a negative effect on the mechanical properties of surimi. It was found that with increase in the level of fish gelatin, the breaking force and deformation of surimi gel decreased (p<0.05). However, there was an increase in breaking force and deformation of surimi gel with 0-15% fish gelatin when microbial trans-glutaminase (MTGase) was incorporated at different concentrations (0-1.2 units/g)surimi as reported by [146] on the gel properties of threadfin bream (Nemipterus bleekerii) surimi. The expressive moisture content of surimi gel was also found to be decreased. The effects of gelatin films enriched with laurel leaf essential oil on the quality of rainbow trout (Oncorhynchus mykiss) during refrigerated storage at (±1) °C were studied over a period of 26 days. The results on pH, total volatile base nitrogen (TVBN), thio-barbituric acid (TBA), free fatty acid (FFA) and peroxide value (PV) analysis, and colour measurement showed that the gelatin film enriched with laurel essential oil (1% by volume per mass) was suitable for the preservation of rainbow trout fillet and the ability of laurel essential oil to preserve the film depended on its ratio [147], [148] reported that bio-nanocomposite films prepared from tilapia and squid skin gelatin incorporated with ethanolic extract from coconut husk treated onmackerel meat powder helps to maintain quality and extend the shelf-life. [149], studied the effect of gelatin based coating solutions enriched with natural preservative agents like chitosan, garlic (Allium sativum) and lime (Citrus aurantifolia) on quality and shelf life of refrigerated fresh Indian salmon (Eleutheronema tetradactylum) fillets for antimicrobial activity against eight fish-borne pathogens and spoilage. The coating formula was used by dip treatment of Indian salmon fillets and found to be highly efficient in extending the shelf life up to 16 days in refrigerated storage.

**Conclusion**

The good film-forming and biodegradable properties of proteins make the protein-based films become one of the important areas in the research of food packaging materials. The film-forming ability of each protein is slightly different due to their different physical and chemical properties. Plasticizers are mostly added to improve the elasticity in the production process. The protein-based films have moderate to good mechanical properties and oxygen barrier properties, but are sensitive to moisture barrier properties. Physical or chemical treatment methods can be applied improve the properties of protein-based films for specific applications. Different food has different storage requirements which require specific packaging materials to meet specific storage conditions. Protein-based biopolymer materials could be a main candidate to meet the requirements of various food packaging materials through modification due the nutrition and biodegrade. Study on the relations between the function, structure and composition of protein-based films will give information on the methods and film modification required so that the protein-based films is suitable for food packaging to increase its functional properties. Active packaging is promising for the rapid development of the functional food market. The active properties i.e. antioxidant and antimicrobial properties of protein-based films selected based on the food characteristics and storage requirements, can effectively inhibit or delay the growth of microorganisms and the oxidation of lipids thereby ensuring food safety and prolonging the shelf life of food.

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