

# Methods for the Improvement of Barrier $1 \mathbf{X}$

and Mechanical Properties of Edible Packaging

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## Abstract

Packaging is an indispensable fragment to preserve quality characteristics and improve storage, transportation and marketing of food products. Increased health interests in nutrition, safety and environmental issues have led to the development of edible packaging. Edible packaging developed from agro-industrial byproducts and wastes has always been a trend. Recent studies have shown reduction in the environmental wastes caused due to the non-biodegradable food packaging. Diverse edible packaging materials developed have barrier properties towards the transfer of oxygen and moisture and have been successfully used to replace synthetic polymer-based films. Much attention acquired by edible packaging is due to increased shelf life, enhanced mechanical properties, enrobing heterogeneous foods and preserving organoleptic characteristics. Biopolymers like pure starch find their way to be used for the development of films. Films produced from starch are hard with poor mechanical properties and are also difficult to handle due to high water sensitivities. Various methods have been employed to mitigate the shortcoming of films that are based on starch and involve its modification by physical, chemical and biological techniques. Modification changes the cross linkages of starch and addition of certain nontoxic

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functional additives. Research on techniques for the amelioration of mechanical and protective properties of these films which are edible in nature has endured rapid expansion in the past years. The current study envisages the methods and techniques for the improvement of characteristics of edible films.

#### Keywords

 $Biodegradable \cdot Edible \cdot Films \cdot Modification \cdot Starch$ 

# 18.1 Introduction

Edible packaging materials such as films and coatings have gained popularity among food researchers, scientists and industries due to their inherent biodegradability and edibility as they can be directly consumed and thereby reducing waste disposal problems. Furthermore, they provide excellent barrier properties and enhance the overall quality of food products (Bourtoom 2008). Important factors taken in consideration while selecting materials for development of edible food packaging includes; their ability to improve processing and preservation techniques, their performance as a barrier to environment and excellent carrier of bioactive compounds. Generally, edible films work as an effective moisture barrier and they have the ability to prevent moisture exchange between food materials and surroundings, thus inhibiting undesirable enzymatic and chemical reactions, textural changes and microbial growth (Janjarasskul and Krochta 2010). These packaging films are likely to be capable of preserving the quality and enhancing the keeping quality of oxygen-sensitive food, therefore they can also work as a good oxygen barrier. Carrageenan and chitosan based edible film are the effective barrier to non-polar aroma compounds, inhibiting oxidation and loss of aroma (Hambleton et al. 2009a. **b**). Edible coatings based on hydrocolloid for example carboxymethylcellulose (CMC) and alginate also helps in keeping the internal moisture of the product intact and reducing uptake of fat in fried foodstuffs which have been deep-fried (Dragich and Krochta 2010). Selective permeability of edible materials can help in restricting aroma and flavor loss at the time of freeze-drying operations, whereas during brine-freezing operations, materials having high water vapor permeability can help in reducing salt migration into food (Janjarasskul and Krochta 2010). While selecting the various materials for the formulation of these edible packaging films, an important aspect of it being an excellent carrier of antioxidant or antimicrobial compounds and also its ability to restrict the migration of molecules from the edible package to the food product is highly considered for its various food product applications. There have been various researches in this area of edible materials for the preservation of food due to their good delivery properties. There are various advantages of edible films such as reduction of waste and solid disposal problems, enhancing organoleptic properties like color and sweetness and enhancing the nutritional values of food products by supplementation. Edible films are environment friendly as they can be fully consumed or can be biologically

degraded or recycled. These edible films can be used in the form of an interface between the various layers of the food product which are heterogeneous in nature so as to prevent it from being deteriorated like in the case of strawberries. These films can be used as carriers of antimicrobial or antioxidant species and can also be used for the purpose of microencapsulation of flavoring agents. There are also various functional properties of these edible films such as retarding moisture migration in fruits and vegetables which are wax coated, retarding gas permeability of carbon dioxide and oxygen, retarding solute transport as well as oil and fat migration. Edible films also carry food additives, retain volatile flavor compounds, improve mechanical handling properties of food and enhance the nutritive value of food. The desired characteristics for the formulations of these films and coatings which are edible in nature depends majorly on its application on the food product which is getting coated. Therefore, for oxidation sensitive food products, low oxygen permeability is required.

There are various sources of edible films such as:

- 1. Proteins: Pea protein, Soy protein, wheat gluten, whey protein, casein protein, corn zein, collagen and gelatins, fish myofibrillar protein, egg white protein, peanut protein.
- Polysaccharides: Starches and modified starches, pectins, kefiran, chitin and chitosan, Galactomannans, Cellulose & modified cellulose, Carrageenan, Xanthan gum, Gellan gum, Alginate, Pullulan.
- 3. Lipids: Oils, Free fatty acids, Carnauba wax, paraffin, beeswax, Shellac resin, Acetoglycerides, Terepene resin.

# 18.2 Applications of Edible Packaging Films

## 18.2.1 Oxygen Barrier

There are various reasons for food deterioration such as lipids oxidation and oxidation of food ingredients, enzymatic browning of fresh-cut produce or myoglobin discoloration in fresh meat cuts. Edible films with low oxygen permeability help in preserving the food quality and extending the keeping quality of oxygen sensitive food products while decreasing the usage of non-recyclable plastics. At low relative humidity (RH), the edible films which are based on the hydrocolloidal property mostly have excellent resistance towards gas. In case of high relative humidity (RH) due to the effect of moisture absorption, hydrophilic EVOH film and hydrocolloid-based films are plasticized, this results in the gradual reduction in the resistance or barrier properties of the edible films (Janjarasskul and Krochta 2010).

#### 18.2.2 Moisture Barrier

The migration of moisture from the atmosphere to the food product can be inhibited by the use of modified edible films. Undesirable alterations in the texture of the food product, microbial growth, deteriorative enzymatic and chemical reactions can occur as a result of the alterations in the water content of the packed foods. It has been observed that edible films which are based on the hydrocolloidal properties have higher permeability of water vapor as compared to films prepared by plastics and edible waxes. WVP of hydrophilic films increases at high plasticizer concentration and high relative humidity (RH) due to their significant polarity. Therefore, only in the case of protection of food from moisture migration of food with low moisture content, these films can be used effectively as protective barriers for a short duration of time. Whereas, lipids or any other hydrophobic compounds have low polarity, dense-structured molecular matrixes and low water affinity, therefore they are generally used to prepare moisture barrier coatings or increase the moisture barrier properties of hydrocolloid-based edible films (Janjarasskul and Krochta 2010).

# 18.2.3 Aroma Barrier

It is extremely important to restrict the loss of characteristic flavor and aroma of the food product which are volatile in nature and the inclusion of off-flavor from the atmosphere into the packaged food during their distribution as well as the storage. In the case of low diffusivity of the compound that is migrating through the polymer matrix and low affinity to film materials, the barrier property of the packaging film is developed. These edible films having the polysaccharides with hydrophilic nature makes them an excellent barrier to the compounds that cause the aroma of the food product which are non-polar in nature. Therefore, the flavor and aroma encapsulation with the help of carbohydrates and protein-based emulsion films were proposed (Rosenberg and Lee 2004; Pegg and Shahidi 2007; Hambleton et al. 2009a, b). Preservation of the active ingredient in the dispersed phase which is non-polar in nature or the aroma compounds which are organic and hydrophobic in nature is the sole objective of this technology. The oxidation of the food product or its aroma loss is prevented by the matrix which is made up of a polymer having hydrophilic properties. When compared with the calculations and measurements of gas and moisture migration, the permeability of aroma compounds is limited and relatively challenging. Various methodologies for the determination of aroma permeability were also proposed (Debeaufort and Voilley 1994; Miller and Krochta 1998).

## 18.2.4 Oil Barrier

Grease resistance can be provided by edible packaging to any lipid-containing products. There is limited data to the quantitative information of the permeability of oil (Krochta 2002). The property of grease-resistance is expected to be shown by

the inherent hydrophilicity of carbohydrate and protein-based polymer films. Examples include whey protein (De Mulder-Johnston 1999) and zein (Trezza and Vergano 1994) were observed to have excellent grease resistance ability.

# 18.3 Methods of Improvement

Films made from proteins are promising biomaterials since they are excellent gas barriers. However, protein films have certain limitations like poor resistance to moisture and water vapor due to their moisture absorbent nature and lack of mechanical strength. The method of cross-linking is an effective method to improve cohesion, mechanical strength, rigidity, water resistance and moisture restrictive property. There can be a usage of several functional groups of proteins to accomplish this. A broad spectrum of various active compounds can be interacted using protein networks. The various functional groups present on the side groups of it which are reactive in nature can do this. Functional properties of films are enhanced by modifying it via physical, chemical or enzymatic cross-linking.

## 18.3.1 Physical Modification

#### 18.3.1.1 Casting

The commonly used technique for formation of a film in laboratory as well as pilot scales is casting method or also known as solvent casting. It involves three steps for the development of a film from biopolymers; firstly, suitable solvent is taken to solubilize biopolymer followed by the solution being casted in the mold itself and finally its drying takes place (Rhim et al. 2006). The specific polymer or the whole polymer mixture is being selected and this marks the initiation of the formulation of these edible films. The polymer which is chosen is dispersed or dissolved in a solvent which is fitting to it; like soy protein isolate polymer is dissolved using ethanol (Jensen et al. 2015); which is termed as solubilization. The polymers ability to solubilize is the main factor on which solvent casting of film formation is dependent upon, rather than its melting (Koide et al. 2013). During casting, glass plates coated with Teflon are used where the obtained solution is poured. The process of drying provides enough duration for the solvent to vaporize which results in the attachment of the polymer film to the mold. Air dryers such as vacuum dryers, tray dryers, microwave and hot air ovens are used for the casting of films so that the solvents can be easily removed (Cha-um et al. 2003). For the casting of edible films, the process of air-drying is a crucial step which helps in formulating an edible film with advantageous microstructure as well as improving the various interactions in the polymer chains (Sherrington 2003). Quick-drying methods applied for casting has resulted in undesirable outcomes on structural and physical properties (Velaga et al. 2018). For the development of edible films, there have been quite some studies on the various relations being the air-drying temperatures and methods (Kaya and Kaya 2000; Tapia-Blacido et al. 2013). Developed edible film should be consistent and

does not have any imperfections such as non-consistency, mechanical harm and inclusion. The most essential parameters of edible films include transparency, thickness, opacity, thermal stability, swelling degree, physical strength as well as the ability to transport oxygen and moisture along with its biological characteristics (Skurtys et al. 2011; Kanatt et al. 2012; Khanzadi et al. 2015). The formation of an easily peeled edible film is done with the help of plasticizers and cohesive matrix which results in excellent barrier properties, mechanical strength, uniform microstructure and thermal stability (Park et al. 2008; Fakhouri et al. 2013). Owing to the significant increase in the quantity of plasticizers, there has been a positive impact on the mechanical strength, thermal properties and barrier properties of the edible film (Sothornvit and Krochta 2005; Sanyang et al. 2015).

#### 18.3.1.2 Extrusion

Extrusion method is a crucial technique for the processing of polymer provided it is presently in application at commercial scale for producing polymeric films (Hernandez-Izquierdo et al. 2008). It improves the physicochemical properties and varies the structure of extruded products (Fitch-Vargas et al. 2016). Extrusion is generally classified into three categories: first, the zone in which the materials to be processed is fed, then the zone in which these fed materials are being kneaded and finally the zone in which the kneaded material is heated (Hauck and Huber 1989; Calderon-Castro et al. 2018). When the process initiates, the components of the mix are carried into the first zone and then are further. This process is also called a dry process as it works best with a minimum amount of solvent or moisture content. Plasticizers are needed during this process to enhance and increase the flexibility of the film (Peressini et al. 2003). The plasticizers which are extruded are polyethylene glycol or sorbitol which is generally used in a measure of about 10% to 60% weight for weight. The ingredients are passed into the kneading zone wherein the density, strain, and temperature of the mixture increases. To develop extruder-based edible film, the thermal energy (extruder barrel temperature) and mechanical (specific mechanical energy) are involved in this method (Fitch-Vargas et al. 2016). It was reported by (Wojtowicz et al. 2015) about the effect which the speed of the screw had on the specific mechanical energy. The various properties of starch-based films like shear rate, shear stress, and homogeneity are affected by the variations in the screw speed of the extrusion. They also control the time of residence and facilitate the addition and removal of the additives like stabilizers. Due to the increase in the speed of the screw, the torque value of the edible films which were based on starch was decreased (Su et al. 2009; Calderon-Castro et al. 2018). According to a study, after a duration of about half an hour and 2 min, the required specific mechanical energy for extrusion of cassava starch ranged from 242.73 to 56.81 KJ/Kg respectively at 150 rpm having a moisture content of about 30% (Fayose and Agbetoye 2012). The thermal energy usually is between the ranges of  $120-170 \,^{\circ}\text{C}$  (Pandit et al. 2018). This technique requires high pressure of about 200 bar for the mixing as well as for the desirable shape of the ingredients (Hanani et al. 2012). Various factors such as reduction in the water level conditions and the thermoplastic behavior of polymers when the glass transition temperature is surpassed during plasticization and heating. Multi-layer films can also be formed by the technique of co-extrusion and can also provide flexibility in order to attain necessary and satisfactory properties of these edible films. The structure of the film with multilayers developed along with the improvement in the functionality and processability of the films are developed by these multilayers in the edible films (Winotapun et al. 2019).

#### 18.3.1.3 Antimicrobial Nanostructure Based Edible Films

The usage of antimicrobial compounds and nanostructures for the formulations of various food packages have been extensively studied upon (de Azeredo 2013; Sung et al. 2013). Major health related concerns are caused due to the inclusion of active compounds which are undesirable in nature from the contact materials of food to the matrix of the food. It is important to consider all of the components of edible packaging materials as a component of the food, given that the entire food can be consumed resulting in no harmful outcomes (de Azeredo 2013). Nano encapsulated antimicrobial peptides and nano-emulsions containing essential oils are the two basic methods of incorporating components having antimicrobial properties into the polymer matrices of the food that is being used to formulate films which can be both edible as well as have antimicrobial properties. Nano-emulsions are majorly used for its property of being antimicrobial and further the encapsulation of essential oils which are of plant origin to enhance shelf life and increase food safety (Pathakoti et al. 2017). Various other bioactive compounds like carotenoids, quinones antioxidants, fatty acids and phytosterols are also incorporated into these edible films (Salvia-Trujillo et al. 2017). Furthermore, they should possess the ability to be included in the edible films so as to produce active food packaging systems. According to a study, the edible based films showing antimicrobial activity based on hydroxypropyl methylcellulose (HPMC) contained as essential oil named Thymus daenensis against a spectrum of fungus as well as bacteria. The scientists illustrated that focusing on the origin of these essential oil (in other words, cultivated or wild T. daenensis), as a result more efficient antimicrobial films were developed against certain specific microorganisms due to their varying compositions (Moghimi et al. 2017). In a study, edible films were produced based upon less or more methyl ester pectins and cinnamaldehyde incorporated papaya puree with nano-emulsions of different sized droplets. Smaller droplets create great inhibition zones result in increased efficiency of antimicrobial activity against pathogenic and bacteria which cause spoilage of food products because of their high bioavailability as well as surface areas (Otoni et al. 2014a). In continuation with this observation, a study also reported that increase in efficiency of antimicrobial activity of edible films based on methylcellulose when these were incorporated by nano-emulsions of oregano and essential oils from clove bud as compared to that of coarse emulsified films (Otoni et al. 2014b). Similar results were observed for different other materials as well (Gul et al. 2018).

#### 18.3.1.4 Irradiation

There has been an immense usage of irradiation technique in order to improve the properties of edible packaging films. Both barriers as well as mechanical properties

of edible films based on proteins were improved effectively by inducing crosslinking through irradiation method. The protein content of these films are generally affected by irradiation which causes rupture of covalent bonds, oxidation of amino acids, formation of protein free radicals, conformational changes and rupture of covalent bonds. Proteins can be converted into higher molecular weight aggregates by the formation of electrostatic, hydrophobic interactions, development of disulphide bonds as well as inter-protein cross-linking reactions (Davies and Delsignore 1987). The molecular properties of proteins can be modified by superoxide and hydroxyl anion radicals which are formed by radiation of film-forming solutions. The cross-linkages which are covalent in nature are developed in the solution of protein due to irradiation and these can further modify and improve the protein films (Garrison 1987).

It has been suggested that the genesis of aggregates of high molecular weights are negligible at the range of low-doses, but gradually increases at higher doses. Improvement in protein films by irradiation treatment like gamma irradiation has been immensely used to improve and develop the proteins. Gamma irradiation cross-linking helps in improving the chemical stability and the water vapor permeability of milk protein based films (Ouattara et al. 2002). There was an increased resistance to enzymatic and microbial biodegradation and significant decrease in the water vapor permeability due to gamma irradiation. It has also been observed that the film forming solution had an increased high molecular weight protein concentration. The researchers pointed out that the effect on gamma irradiation can be explained by two hypotheses. The first hypotheses being the presence of more molecular residues in intermolecular interactions when used in proteins with varying physico-chemical properties and the second being the formation of intra- and/or intermolecular covalent cross-links in the film-forming solutions.

A study investigated that gamma irradiation causes various effects on mechanical properties of milk proteins. The gamma irradiations-initiated formation of a structure of protein gel which was finely stranded. Due to this, the viscosity of proteins film solutions which have undergone the process of irradiation was enhanced compared to that of control films (Ciesla et al. 2004). It was seen that there was significant improvement in the  $\beta$ -conformation as compared to non-irradiated milk proteinbased films due to application of gamma irradiations. Furthermore, due to the presence of protein conformations which are correctly ordered in the gels derived from irradiated solutions, the formation of more crystalline films takes place. As a result, these films show excellent mechanical strength, increased rigidity and improved barrier properties when compared to solutions which were not irradiated.

Lee et al. (2005) reported that a significant amount of disruption was found in the protein molecules which had ordered structures when treated with gamma irradiation. It changed the tensile strength as well as the elongation at break. Further it also improved its water vapor permeability. Since there is an increased accumulation of polypeptide chains, the tensile strength also increases significantly. Therefore, it is observed that the reduction in diffusion rate through the film caused the decrease in water vapor permeability of the edible film.

The various properties of mechanical strength and water resistance of corn protein-based films can be modified by the application of gamma irradiation (Soliman and Furuta 2009). The physicochemical properties of zein based edible films are potentially modified with the help of gamma irradiation treatment, specifically the properties of moisture resistance. The absorption of water molecules into the film was done by its treatment with proteins having high molecular weight procured from cleaved polypeptide and disaggregated protein particles and the diffusion through these films can be reduced by the formation of the earlier mentioned linkages.

## 18.3.2 Chemical Modifications

The film forming properties can also be improved using treatments with chemicals like alkali, acid or cross-linking agents. Less permeability and greater tensile strength were obtained when there is an increase in the protein structure interaction. It was observed by (Gennadios et al. 1993) that when the isolate of soy protein is subjected to an alkaline treatment, the oxygen permeability, tensile strength and water vapor permeability remained unaffected, but appearance of the film was improved by making it more uniform and clear and also reduction in the occurrence of air bubbles along with break at the elongation. Various chemical agents like aldehydes such as glutaraldehyde, formaldehyde or gloxal are used for the purpose of protein's covalent cross-linking.

Formaldehyde has extensive reaction specificity and is considered as the simplest of cross-linking agents. It reacts with the side chains of tyrosine, cysteine, tryptophan, arginine and histidine in addition to amine group of lysine. Formaldehyde can cross-link due to its property to react bi-functionally. It was seen that formaldehyde was less specific than glutaraldehyde. Glutaraldehyde was able to react with cysteine, tyrosine, lysine and histidine (Kim and Tae 1983). Lysine and arginine side chain groups are involved in the protein cross-linking by glyoxal (Marquie 2001) at alkaline pH. In general, there are two step processes taking place during the reaction between protein and formaldehyde. There is the formation of methylol compounds in the first step and formation of bridges of methylene which act as cross-links between the various protein chains in the second step.

The usage of aldehydes and their various effects of cross-linking for the development of glutenin-rich films were studied by Hernández-Muñoz et al. (2004). The water vapor permeability values decreased by around 30% when glutenin rich films were incorporated by cross-linking agents like glutaraldehyde, glyoxal and formaldehyde. With help of formaldehyde and glutaraldehyde, the highest tensile strength values were achieved. In addition, with the usage of cross-linking agents, the glass transition temperature of cross-linked films was seen to shift from its original value. Due to this reason glutaraldehyde and gossypol proved to be less efficient than formaldehyde in cross-linking. While synthesizing biodegradable materials, the tendency of it being toxic must be considered. There should be a permanent protein network formed by cross-linking when any aldehyde is used. Also, the outcome of the aldehyde used during this process on the environment at the termination of the material's life should be considered.

The properties of sunflower protein isolate made thermo-molded films showed various changes due to the effects of cross-linking agents which are found naturally such as tannins and gallic acid. It was studied that higher mechanical properties were resulted by the incorporation of gallic acid and tannins than for control films, but were lower than the films obtained with aldehydes. Weak interactions can cause these contrary to the covalent bonds as in the case of aldehydes (Orliac et al. (2002).

The mechanical properties of gelatin films were improved with the help of tannic acid and ferulic acid, (Cao et al. 2007). It was seen that tannic and ferulic acid had an effect of cross-linking on the gelatin film and therefore acted as natural cross-linking agents. When the pH value of the film-forming solution was 9 for the tannic acid and 7 for ferulic acid, the gelatin-based films showed the maximum mechanical strength. In addition, after the storage for more than 90 days, the properties of gelatin films treated by tannic acid can become better; while the storage time had lesser effect on ferulic acid-modified films.

Hydroxypropyl methylcellulose (HPMC) films are incorporated by preparing nanoparticles of chitosan/tripolyphosphate (CS/TPP)). The film mechanical and barrier properties were improved by the incorporation of nanoparticles of chitosan. The HPMC had various empty spaces in its pores which tend to be occupied by the chitosan nanoparticles, which thereby increases the collapse of the pores and thus improve the film tensile properties and water vapor permeability. With the addition of nanoparticles there is an increase in thermal stability. The study by de Moura et al. (2009) investigated the use of CS-TPP nanoparticles to strengthen the HPMC films. In the last decade, various research programs have concentrated their word on the development of better edible coatings and films (Denavi et al. 2009; Sebti et al. 2007). Amongst these, chitosan and hydroxypropyl methylcellulose (HPMC) which are polysaccharide polymers are closed studied upon (Hernández Muñoz et al. 2008; Perez et al. 2008; Dogan and McHugh 2007). To enhance the quality and shelf life of food products of seafood, agriculture and poultry origin, the various applications of chitosan were discussed in the study by No et al. (2007). However, when solubilized into foods containing high water activity and a reduction in the resistance of these films due to their hydrophilic nature, discourages their applications on an industrial level (Bertuzzi et al. 2007). The amalgam of films with sucrose palmitate, HPMC and sorbitanmonostearate was reported by Villalobos et al. (2006). With a help of a hydrocolloidal to surfactant ratio, the permeability property of moisture for these films was decreased. Syntheses of these films formulated with pectin and polypropylene (PP) was found in a study by Elsabee et al. (2008). Chitosan can form various complex compounds and this property was used to construct a firm multi-layered form on the surface of the PP film, to form a film of increased antimicrobial properties which are used to formulate materials for packing of crops after their harvest. The method was quite successful in which specific polyanions were ionically cross-linked with cationic chitosan. However, it had its complexity with negatively charged polymers. Upon the contact with multivalent polyanions, chitosan has the ability to rapidly form gel caused by the emergence of crosslinkages of inter- and intramolecular type which are arbitrated by these polyanions. Tripolyphosphate is the most popular one among some polyanions that were studied. This is due to its property to be non-toxic and ability to form gel relatively faster. Some interesting features are being exhibited by the CS-TPP nano system which makes them reliable transporters of macromolecules (Gan et al. 2005). Chitosan tripolyphosphate infused hydroxypropyl MC films could be a used material for the application of food packaging applications for the purpose of extension of the storage life of food materials. There can be expansion in the usage of edible films of biodegradable types by the application of nanocomposites (Lagarón et al. 2005; Sinha Ray and Bousmina 2005; Sorrentino et al. 2007). Composites of polymer which have low molecular weight and loadings are fortified due to the restriction of chains within these nanocomposites by the restricted field present among the sheets of the films (Orts et al. 2005; Usuki et al. 1995). Improvements in mechanical properties and the decrease in gas and liquid permeability was resulted by the combination of arrangement of nanoparticle or nanostructure, robust interactions of the surface and chain confinement. The nanoparticles of CS and TPP were formulated and infused into the HPMC films.

CS/TPP nanoparticles in hydroxypropyl methylcellulose edible films ameliorated their barrier and mechanical properties. The thermal characteristics of the films were modified by the nanoparticles in HPMC films (Du et al. 2008). Coatings of chitosan on strawberries reduced the physical damage caused during processing, transportation and finally its storage. However, owing to the sturdy adhesive type density of the energy index of carbohydrate and protein-based edible materials; they tend to have less tensile strength. The flavor and appearance of the food product is also enhanced by these appealing edible coatings. The fruits (such as apple, lemon and oranges) have waxes on them which polishes the surface and gives a glossy appearance. It also decreases the spoilage of a product which is caused by high moisture content by acting as a moisture barrier for it (Lin and Zhao 2007).

In a recent research by (Ghanbarzadeh et al. 2011), the combination of the individual effects of carboxymethyl cellulose and citric acid was used to ameliorate the physical and resistive properties of corn starch-based edible films. The relationship between the carboxyl group of CA and the hydroxyl group on the starch resulted in multi-carboxylic structure. This interaction helps in improving its barrier to moisture because of decreasing the free OH groups of starch. The CA concentration was raised from 0 to 10% weight by weight and this significantly improved the ultimate tensile strength (UTS) and water vapor barrier property (p < 0.05).

Carrot basically consists of substances made of cellulose, water, protein and pectin (Bao and Chang 1994) and these earlier mentioned materials may help in providing desirable properties to form biodegradable, renewable and economical packaging films. In a study, gelatin, carboxymethyl cellulose (CMC) and starch were added to carrot-based films which may help in improving their strength by creating a synergistic effect. Gelatin that is derived from partial degradation of collagen is used as edible films due to its biodegradability, myriad and excellent gelling properties (Cao et al. 2007; Dangaran et al. 2009).

## 18.3.3 Enzymatic Modifications

Amongst the various methods for improving the barrier properties and mechanical strength of the edible films, one effective technique is using enzymatic methods for a cross linking. Enzymes like polyphenol oxidase, transglutaminase, lysyl oxidase, peroxidase and lipoxygenase have been used since a long time for the cross linking of proteins. However, high molecular weight (MW) bio-polymers can be formed by the action of an enzyme called transglutaminase. The transglutaminase enzyme catalyzes the reactions of acyl transfer between the  $\lambda$ -carboxyamide groups of glutamine residues which is and acyl donor and  $\varepsilon$ -amino groups of lysine residues which is an acyl acceptor and results in emergence of inter and intramolecular cross-linked proteins of  $\varepsilon$ -( $\lambda$ -glutaminyl) lysine DeJong and Koppelman (2002).

Various sources of proteins for example gelatin, soy and casein proteins were studied upon for polymerization using transglutaminase where various reactions in the strength of the gel were dependent on the different sources of proteins and the reaction (Sakamoto et al. 1994). The intensity and order of the gel of these proteins influence their strength which helps the enzymes to produce the required cross-links. The occurrence of hindrance to the physical cross-linkages by the new covalent linkages depends on the formation of the triple helix and the process of renaturation during the gel formation (Babin and Dickinson 2001). Films acquired from slightly deamidated gluten had high chances of formation of covalent bonds by transglutaminase Larre et al. (2000). The tensile strength of protein films is improved by the cross-linkage of transglutaminase which decreases the solubility properties and its elongation at break.

It is still undetermined that enzymatic modification by the use of cross-linking can enhance and modify the film forming properties. The types of substrate proteins or amount of enzyme used are the various processing parameters and factors on which the enhancement in the edible films properties which are protein-based. The enzyme concentration is also affected along with the improvement in the properties of edible film. In a study on the properties of soy protein-based films, it was reported that the hydrophobicity and tensile strength can be modified and improved with the usage of transglutaminase (Tang and Jiang 2007).

# 18.4 Conclusions

The edible films have various advantages over synthetic ones as they can be used as packaging films which are edible in nature. During these recent years edible films have gained popularity due to their biodegradability and edibility. These films are derived from various biopolymer sources such as protein, carbohydrates and lipids and can be further modified using various physical, chemical and enzymatic techniques. Some of these methods include casting, extrusion, irradiation etc. The presence of unique structures is exhibited by proteins which favors the modification and development of these films. The mechanical properties of such films are far better than that of the fat and polysaccharide-based films. However, these edible packaging films when compared with synthetic polymers show poor water vapor resistance and inferior quality of mechanical strength, therefore, limiting their food packaging applications. The use of various physical, chemical and enzymatic methods can be used to improve these properties of films. The properties of the film that are formed by the application of the earlier mentioned methods depend on the various types of conditions and modification undergone. The properties such as water resistance and mechanical strength are efficiently increased by the help of chemical and enzymatic modifications. Although, toxicity can be caused by the use of aldehydes in chemical modifications of these films. This can cause huge matters of concern in application of chemical modification. Therefore, these advancements in modification as well as development of edible packaging films pose to be highly effective and have promising future prospects to it.

## References

- Babin H, Dickinson E (2001) Influence of transglutaminase treatment on the thermoreversible gelation of gelatin. Food Hydrocoll 15(3):271–276
- Bao B, Chang KC (1994) Carrot juice color, carotenoids, and nonstarchy polysaccharides as affected by processing conditions. J Food Sci 59(6):1155–1158
- Bertuzzi MA, Armada M, Gottifredi JC (2007) Physicochemical characterization of starch-based films. J Food Eng 82(1):17–25
- Bourtoom T (2008) Edible films and coatings: characteristics and properties. Int Food Res J 15(3):237-248
- Calderon-Castro A, Vega-Garcia MO, de JesusZazueta-Morales J, Fitch-Vargas PR, Carrillo-Lopez A, Gutierrez-Dorado R, Aguilar-Palazuelos E (2018) Effect of extrusion process on the functional properties of high amylose corn starch edible films and its application in mango (Mangiferaindica L.) ev. Tommy Atkins. J Food Sci Technol 55(3):905–914
- Cao N, Fu Y, He J (2007) Mechanical properties of gelatin films cross-linked, respectively, by ferulic acid and tannin acid. Food Hydrocoll 21(4):575–584
- Cha-um S, Mosaleeyanon K, Kirdmanee C, Supaibulwatana K (2003) A more efficient transplanting system for Thai neem (Azadirachtasiamensis Val.) by reducing relative humidity. Sci Asia 29:189–196
- Ciesla K, Salmieri S, Lacroix M, Le Tien C (2004) Gamma irradiation influence on physical properties of milk proteins. Radiat Phys Chem 71(1–2):95–99
- Dangaran K, Tomasula PM, Qi P (2009) Structure and function of protein-based edible films and coatings. In: Edible films and coatings for food applications. Springer, New York, NY, pp 25–56
- Davies KJ, Delsignore ME (1987) Protein damage and degradation by oxygen radicals. III Modification of secondary and tertiary structure. J Biol Chem 262(20):9908–9913
- de Azeredo HM (2013) Antimicrobial nanostructures in food packaging. Trends Food Sci Technol 30(1):56–69
- de Moura MR, Aouada FA, Avena-Bustillos RJ, McHugh TH, Krochta JM, Mattoso LH (2009) Improved barrier and mechanical properties of novel hydroxypropyl methylcellulose edible films with chitosan/tripolyphosphate nanoparticles. J Food Eng 92(4):448–453
- De Mulder-Johnston CLC (1999) Thermal analysis of, and oil migration through films from, whey protein isolate. University of California, Davis
- Debeaufort F, Voilley A (1994) Aroma compound and water vapor permeability of edible films and polymeric packagings. J Agric Food Chem 42(12):2871–2875

- DeJong GAH, Koppelman SJ (2002) Transglutaminase catalyzed reactions: impact on food applications. J Food Sci 67(8):2798–2806
- Denavi G, Tapia-Blacido DR, Anon MC, Sobral PJA, Mauri AN, Menegalli FC (2009) Effects of drying conditions on some physical properties of soy protein films. J Food Eng 90(3):341–349
- Dogan N, McHugh TH (2007) Effects of microcrystalline cellulose on functional properties of hydroxy propyl methyl cellulose microcomposite films. J Food Sci 72(1):016–022
- Dragich AM, Krochta JM (2010) Whey protein solution coating for fat-uptake reduction in deepfried chicken breast strips. J Food Sci 75(1):43–47
- Du WX, Olsen CW, Avena-Bustillos RJ, McHugh TH, Levin CE, Friedman M (2008) Antibacterial activity against E. coli O157:H7, physical properties, and storage stability of novel carvacrolcontaining edible tomato films. J Food Sci 73(7):378–383
- Elsabee MZ, Abdou ES, Nagy KS, Eweis M (2008) Surface modification of polypropylene films by chitosan and chitosan/pectin multilayer. Carbohydr Polym 71(2):187–195
- Fakhouri FM, Costa D, Yamashita F, Martelli SM, Jesus RC, Alganer K, Innocentini-Mei LH (2013) Comparative study of processing methods for starch/gelatin films. Carbohydr Polym 95(2):681–689
- Fayose FT, Agbetoye LAS (2012) Characterizing the specific mechanical energy requirement (SME) of extrudates of cassava and cereals from a locally developed extruder. In Rural Development. International Conference of Agricultural Engineering-CIGR-AgEng 2012: Agriculture and engineering for a healthier life, Valencia, Spain, 8–12 July 2012. CIGR-EurAgEng
- Fitch-Vargas PR, Aguilar-Palazuelos E, de JesusZazueta-Morales J, Vega-García MO, Valdez-Morales JE, Martínez-Bustos F, Jacobo-Valenzuela N (2016) Physicochemical and microstructural characterization of corn starch edible films obtained by a combination of extrusion technology and casting technique. J Food Sci 81(9):2224–2232
- Gan Q, Wang T, Cochrane C, McCarron P (2005) Modulation of surface charge, particle size and morphological properties of chitosan–TPP nanoparticles intended for gene delivery. Colloids Surf B: Biointerfaces 44(2–3):65–73
- Garrison WM (1987) Reaction mechanisms in the radiolysis of peptides, polypeptides, and proteins. Chem Rev 87(2):381–398
- Gennadios A, Brandenburg AH, Weller CL, Testin RF (1993) Effect of pH on properties of wheat gluten and soy protein isolate films. J Agric Food Chem 41(11):1835–1839
- Ghanbarzadeh B, Almasi H, Entezami AA (2011) Improving the barrier and mechanical properties of corn starch-based edible films: effect of citric acid and carboxymethyl cellulose. Ind Crop Prod 33(1):229–235
- Gul O, Saricaoglu FT, Besir A, Atalar I, Yazici F (2018) Effect of ultrasound treatment on the properties of nano-emulsion films obtained from hazelnut meal protein and clove essential oil. Ultrason Sonochem 41:466–474
- Hambleton A, Debeaufort F, Bonnotte A, Voilley A (2009a) Influence of alginate emulsion-based films structure on its barrier properties and on the protection of microencapsulated aroma compound. Food Hydrocoll 23(8):2116–2124
- Hambleton A, Fabra MJ, Debeaufort F, Dury-Brun C, Voilley A (2009b) Interface and aroma barrier properties of iota-carrageenan emulsion–based films used for encapsulation of active food compounds. J Food Eng 93(1):80–88
- Hanani ZN, Beatty E, Roos YH, Morris MA, Kerry JP (2012) Manufacture and characterization of gelatin films derived from beef, pork and fish sources using twin screw extrusion. J Food Eng 113(4):606–614
- Hauck BW, Huber GR (1989) Single screw vs twin screw extrusion. Cereal Foods World 34(11):930-939
- Hernandez-Izquierdo VM, Reid DS, McHugh TH, De J, Berrios J, Krochta JM (2008) Thermal transitions and extrusion of glycerol-plasticized whey protein mixtures. J Food Sci 73(4):169–175
- Hernández-Muñoz P, Villalobos R, Chiralt A (2004) Effect of cross-linking using aldehydes on properties of glutenin-rich films. Food Hydrocoll 18(3):403–411
- Janjarasskul T, Krochta JM (2010) Edible packaging materials. Annu Rev Food Sci Technol 1:415– 448

- Jensen A, Lim LT, Barbut S, Marcone M (2015) Development and characterization of soy protein films incorporated with cellulose fibers using a hot surface casting technique. LWT Food Sci Technol 60(1):162–170
- Kanatt SR, Rao MS, Chawla SP, Sharma A (2012) Active chitosan–polyvinyl alcohol films with natural extracts. Food Hydrocoll 29(2):290–297
- Kaya S, Kaya A (2000) Microwave drying effects on properties of whey protein isolate edible films. J Food Eng 43(2):91–96
- Khanzadi M, Jafari SM, Mirzaei H, Chegini FK, Maghsoudlou Y, Dehnad D (2015) Physical and mechanical properties in biodegradable films of whey protein concentrate–pullulan by application of beeswax. Carbohydr Polym 118:24–29
- Kim CS, Tae GS (1983) Ecological studies on the Halophyto communities at Western and southern coasts in Korea (IV)-the halophyte communities at the different salt marsh habitats. Korean J Ecol 6(3):167–176
- Koide Y, Ikake H, Muroga Y, Shimizu S (2013) Effect of the cast-solvent on the morphology of cast films formed with a mixture of stereoisomeric poly (lactic acids). Polym J 45(6):645–650
- Krochta JM (2002) Proteins as raw materials for films and coatings: definitions, current status, and opportunities. Protein Based Films Coatings 1:1–40
- Larre C, Denery-Papini S, Popineau Y, Deshayes G, Desserme C, Lefebvre J (2000) Biochemical analysis and rheological properties of gluten modified by transglutaminase. Cereal Chem 77(2):121–127
- Lee SL, Lee MS, Song KB (2005) Effect of gamma-irradiation on the physicochemical properties of gluten films. Food Chem 92(4):621–625
- Lin D, Zhao Y (2007) Innovations in the development and application of edible coatings for fresh and minimally processed fruits and vegetables. Compr Rev Food Sci Food Saf 6(3):60–75
- Marquie C (2001) Chemical reactions in cottonseed protein cross-linking by formaldehyde, glutaraldehyde, and glyoxal for the formation of protein films with enhanced mechanical properties. J Agric Food Chem 49(10):4676–4681
- Miller KS, Krochta JM (1998) Measuring aroma transport in polymer films. Trans ASAE 41(2):427
- Moghimi R, Aliahmadi A, Rafati H (2017) Antibacterial hydroxypropyl methyl cellulose edible films containing nanoemulsions of Thymus daenensis essential oil for food packaging. Carbohydr Polym 175:241–248
- Orliac O, Rouilly A, Silvestre F, Rigal L (2002) Effects of additives on the mechanical properties, hydrophobicity and water uptake of thermo-moulded films produced from sunflower protein isolate. Polymer 43(20):5417–5425
- Orts WJ, Shey J, Imam SH, Glenn GM, Guttman ME, Revol JF (2005) Application of cellulose microfibrils in polymer nanocomposites. J Polym Environ 13(4):301–306
- Otoni CG, de Moura MR, Aouada FA, Camilloto GP, Cruz RS, Lorevice MV, Mattoso LH (2014a) Antimicrobial and physical-mechanical properties of pectin/papaya puree/ cinnamaldehydenanoemulsion edible composite films. Food Hydrocoll 41:188–194
- Otoni CG, Pontes SF, Medeiros EA, Soares NDF (2014b) Edible films from methylcellulose and nanoemulsions of clove bud (Syzygiumaromaticum) and oregano (Origanumvulgare) essential oils as shelf-life extenders for sliced bread. J Agric Food Chem 62(22):5214–5219
- Ouattara B, Canh LT, Vachon C, Mateescu MA, Lacroix M (2002) Use of γ-irradiation crosslinking to improve the water vapor permeability and the chemical stability of milk protein films. Radiat Phys Chem 63(3–6):821–825
- Pandit P, Nadathur GT, Maiti S, Regubalan B (2018) Functionality and properties of bio-based materials. In: Bio-based materials for food packaging, vol 81–103. Springer, Singapore
- Park JW, Whiteside WS, Cho SY (2008) Mechanical and water vapor barrier properties of extruded and heat-pressed gelatin films. LWT Food Sci Technol 41(4):692–700
- Pathakoti K, Manubolu M, Hwang HM (2017) Nanostructures: current uses and future applications in food science. J Food Drug Anal 25(2):245–253
- Pegg RB, Shahidi F (2007) Encapsulation, stabilization, and controlled release of food ingredients and bioactives. In: Handbook of food preservation. CRC Press, Boca Raton, FL, pp 527–586
- Peressini D, Bravin B, Lapasin R, Rizzotti C, Sensidoni A (2003) Starch-methylcellulose based edible films: rheological properties of film-forming dispersions. J Food Eng 59(1):25–32

- Perez OE, Sanchez CC, Pilosof AM, Patino JMR (2008) Dynamics of adsorption of hydroxypropyl methylcellulose at the air-water interface. Food Hydrocoll 22(3):387–402
- Ray SS, Bousmina M (2005) Biodegradable polymers and their layered silicate nanocomposites: in greening the 21st century materials world. Prog Mater Sci 50(8):962–1079
- Rhim JW, Mohanty AK, Singh SP, Ng PK (2006) Effect of the processing methods on the performance of polylactide films: Thermocompression versus solvent casting. J Appl Polym Sci 101(6):3736–3742
- Rosenberg M, Lee SJ (2004) Calcium-alginate coated, whey protein-based microspheres: preparation, some properties and opportunities. J Microencapsul 21(3):263–281
- Sakamoto H, Kumazawa Y, Motoki M (1994) Strength of protein gels prepared with microbial transglutaminase as related to reaction conditions. J Food Sci 59(4):866–871
- Salvia-Trujillo L, Soliva-Fortuny R, Rojas-Grau MA, McClements DJ, Martin-Belloso O (2017) Edible nanoemulsions as carriers of active ingredients: a review. Annu Rev Food Sci Technol 8: 439–466
- Sanyang ML, Sapuan SM, Jawaid M, Ishak MR, Sahari J (2015) Effect of plasticizer type and concentration on tensile, thermal and barrier properties of biodegradable films based on sugar palm (Arengapinnata) starch. Polymers 7(6):1106–1124
- Sebti I, Chollet E, Degraeve P, Noel C, Peyrol E (2007) Water sensitivity, antimicrobial, and physicochemical analyses of edible films based on HPMC and/or chitosan. J Agric Food Chem 55(3):693–699
- Sherrington DC (2003) Introduction to physical polymer science. Reactive polymers, vol 20. Wiley, Hoboken, NJ
- Skurtys O, Velásquez P, Henriquez O, Matiacevich S, Enrione J, Osorio F (2011) Wetting behavior of chitosan solutions on blueberry epicarp with or without epicuticular waxes. LWT Food Sci Technol 44(6):1449–1457
- Soliman EA, Furuta M (2009) Influence of  $\gamma$ -irradiation on mechanical and water barrier properties of corn protein-based films. Radiat Phys Chem 78(7–8):651–654
- Sorrentino A, Gorrasi G, Vittoria V (2007) Potential perspectives of bio-nanocomposites for food packaging applications. Trends Food Sci Technol 18(2):84–95
- Sothornvit R, Krochta JM (2005) Plasticizers in edible films and coatings. In: Innovations in food packaging. Academic Press, London, pp 403–433
- Su HJ, Dorozhkin DV, Vance JM (2009) A screw theory approach for the conceptual design of flexible joints for compliant mechanisms. J Mech Robot 1(4)
- Sung SY, Sin LT, Tee TT, Bee ST, Rahmat AR, Rahman WA. Vikhraman M (2013) Antimicrobial agents for food packaging applications. Trends Food Sci Technol 33(2):110–123
- Tang CH, Jiang Y (2007) Modulation of mechanical and surface hydrophobic properties of food protein films by transglutaminase treatment. Food Res Int 40(4):504–509
- Tapia-Blacido DR, do AmaralSobral PJ, Menegalli FC (2013) Effect of drying conditions and plasticizer type on some physical and mechanical properties of amaranth flour films. LWT Food Sci Technol 50(2):392–400
- Trezza TA, Vergano PJ (1994) Grease resistance of corn zein coated paper. J Food Sci 59(4):912–915
- Usuki A, Koiwai A, Kojima Y, Kawasumi M, Okada A, Kurauchi T, Kamigaito O (1995) Interaction of nylon 6-clay surface and mechanical properties of nylon 6-clay hybrid. J Appl Polym Sci 55(1):119–123
- Velaga SP, Nikjoo D, Vuddanda PR (2018) Experimental studies and modeling of the drying kinetics of multicomponent polymer films. AAPS PharmSciTech 19(1):425–435
- Winotapun C, Phattarateera S, Aontee A, Junsook N, Daud W, Kerddonfag N, Chinsirikul W (2019) Development of multilayer films with improved aroma barrier properties for durian packaging application. Packag Technol Sci 32(8):405–418
- Wojtowicz A, Mitrus M, Oniszczuk T, Moscicki L, Kręcisz M, Oniszczuk A (2015) Selected physical properties, texture and sensory characteristics of extruded breakfast cereals based on wholegrain wheat flour. Agric Agric Sci Proc 7:301–308