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Role of Active Food Packaging Developed from Microencapsulated Bioactive Ingredients in Quality and Shelf Life Enhancement: A review

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Abstract: Food spoilage is mainly caused by lipid oxidation which can be delayed by vacuum or modified atmosphere packaging. Recent approaches basically aim to develop active food packaging through addition of antioxidants in edible films that guarantees food safety and quality for extended period of time. This review focusses on the replacement of chemical additives with natural antioxidants such as extracts or essential oils and effects on mechanical, barrier and radical scavenging activities of several films. Bioactive compounds lose their stability under storage conditions therefore microencapsulation is a strategy sustaining their stability, increasing bioavailability, delaying onset of oxidation and hydrolysis under processing conditions. Additives such as emulsifying, anti-browning, antioxidant and antimicrobial agents, colors, spices, plasticizers, surface active agents, nutrients and textural modifiers are also added into films with an aim to modify poor mechanical and barrier attributes of edible films *e.g.* tensile force. Extracts from herbs and essential oils increased the total phenolic compounds resulting in an increased radical scavenging activity. The interaction between film matrix and active groups of additives improved film barrier properties whereas hydrophilic substances depicted an increment in oxygen and water vapor permeability. The morphology of microcapsules was affected by type of biopolymers, ratio and its concentration, corresponding charges, temperature, solidifying as well as cooling rate and pH.
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1. Introduction

Food spoilage is mainly caused by lipid oxidation. High degree of unsaturation in lipid foods makes them highly vulnerable to deterioration imparting them off-flavor, induce oxidative rancidity resulting in product unsuitable for human intake. Besides these, toxic aldehydes and ketones are produced which decline nutritional quality of food products. Different strategies have been implemented to reduce oxidation including packaging technology. Food packaging has just a minor role in shielding and proper commercialization of product. Novelty in intelligent and active packaging have been introduced now-a-days by proposing unique solutions that guarantee food safety and quality for extended period of time. Any material that is utilized in food packaging either in form of film or coating can be consumed with the food product. They have strong barrier properties with great resistance towards oxygen and water. Several additives such as plasticizers, anti-oxidizing and antimicrobial substances, anti-browning agents, colors, flavors and spices have been added resulting in increased organoleptic traits and retaining product quality. Additionally, the ecological influence inside the product is low as a result of limited external packaging.

Owing to the target of reducing usage of chemical additives in food industries, a great concern towards substitution of chemical additives with natural ones has developed in food processors. The film coating around fresh-cut vegetables and fruits had been studied by Rojas-Grau *et al.* (2009). Essential oils has higher antimicrobial efficiency which symbolize as the best ingredient for active food packaging. EO's together with anti-browning agents like potassium sorbate or sodium benzoate to prevent enzymatic browning in minimally processed fruits and vegetables had also been studied by Chamorro *et al.* (2011).

Degradation of antioxidants in atmospheric oxygen can be prevented through encapsulation technique. Thus, microencapsulation with an appropriate carrier is an alternative technology for enhancing the storage and environmental stability of bioactives as well as giving an advance to mask off-flavour, bitter taste and astringency of polyphenols. Consequently, the effects of encapsulation on food antioxidants has gained a significant value. Microencapsulation is a technique which includes the protection of active ingredients such as solid, liquid and gaseous materials by a layer of encapsulating material to form microcapsules µm to mm in size. There are three types of techniques such as physical, chemical and physicochemical methods. In physicochemical, a sequence of colloidal phenomena that include aqueous phase separation of solo or a merger of two complementary charged biopolymers is called coacervation. Considering the chemical (dispersion, interfacial, emulsion polymerization) and physical (crosslinking, coacervation, spray drying) techniques, spray drying is the method employing for drying used in microencapsulation of different products (Neto *et al.,* 2019). Therefore, the objectives of this review article is to update the information about production of edible films and coatings as carriers of antioxidants and its encapsulation through coacervation technique.

2. Natural antioxidants

Antioxidants added in food with the purpose of delaying rancidity and their presence is strictly considered on account of some risks associated with it. Alternatively, the natural antioxidants especially plant extracts, α-tocopherol and essential oil can be used in place of synthetic antioxidants. It is also noteworthy that wastes from food industry have potential source of antioxidants (Barbosa-Pereira *et al.*, 2013). Herbs and spices have high amount of phenolic substances having high hydrogen donating activity. These are thyme, oregano, rosemary and marjoram which belong to family *Lamiaceae* and incorporated in foods for their flavor and retarding oxidation. Another herb of family *Theaceae*, tea, has high possibility of containing natural antioxidants. They are utilized in the form of essential oil, extract or oleoresin (Nakagawa *et al.*, 2011).

2.1. Essential oils

Essential oils are produced in chemical reaction, the mixtures comprised of functional groups and extracted by distillation of steam, through mechanical means or use of inorganic solvent and supercritical carbon dioxide (Tsimogiannis *et al.*, 2017). Selection of technique relies upon the raw material and counted in one of some factors that decide the output and quality of EO's. They compose of lipophilic and volatile compounds that are actually hydrocarbons resulting from the metabolic activity of amino and fatty acids and phenylpropanoids (Tongnuanchan and Benjakul, 2014). The recovery of essential oil from aromatic herbs and spices is achieved by steam distillation. They are feasible to use as antimicrobial agent but they also have possibility to act as natural antioxidant. The components that are highlighted as antimicrobial constituents are thymol and carvacol, which also exhibit average antioxidant potential (Ganiari *et al.*, 2017).

Extracts of the most herbs species and spices contain high phenolic content (TPC) and are extracted by means of solvents or mixed with water. The following features can exert influence on resultant yield such as type of solvent, retention time, temperature, number of washings and solvent to sample ratio. Beyond that, the phenolic content vary from sample to sample and mainly rests upon plant matter and active constituents. The generally used solvents are methanol, ethyl acetate, acetone, water and their miscellaneous combinations. Apolar or non-polar molecules like terpenoids are recovered by ethyl acetate and acetone whereas phenolic acids (rosmarinic) are recovered by water, alcohol and hydro-alcoholic combinations (Oniszczuk *et al.*, 2014).

2.2. Oleoresins

In addition to above these herbs and spices also release oleoresins that are lipophilic and non-volatile *e.g.* waxes and resins (Singh *et al.*, 2014). They are insoluble in water but soluble in organic compounds. On the whole, they are terpenoids and consist little traces of volatile phenolic substances and resin acids. They can be restored by polar or non-polar solvents via hexane and super critical CO_2 (Rajamma *et al.*, 2012). The by-products of plant such as barley husk and peel of pomegranate can also serve as source of antioxidants. The process employs raw materials, subjected to hydrolysis by acid and further undergo alkaline treatment with the purpose of releasing phenolic complexes from wood components like fibers and lignin (De-Abreu *et al.*, 2012).

3. Active packaging

It is interpreted as a packaged system that integrates ingredients from different sources, which have to absorb or discharge substances at target place whether inside the packed food or outside the environment enclosing food to prolong the shelf life or improve the physical condition of food (Yuan *et al.*, 2015). The role of antioxidants in food packaging is of higher concern for food manufacturers and there are two mechanisms of action: their release inside the food and removal of unwanted constituents from the hollow space or from food as for example metal ions, oxygen and radical oxidative species (LaCoste *et al.*, 2005). All the undesirable substances are entrapped by scavengers engaged in initiation of oxidation. The package must be structured in such a way to permit the release of pre-oxidant constituents to the site where scavenging agents are added. As far as releasing property of antioxidants is concerned, one of the advantages of using packaging system farther than direct incorporation into food, is that they discharge substances in a controlled manner regardless of the continual use of antioxidants during storage interval (Marcos *et al.*, 2014).

4. Use of edible films

The films are pre-manufactured like thin sheets made from edible components whereas edible coatings result in the formation of thin layer around the food material. Coatings are applied in the form of liquid mostly by dipping in liquid mixtures whilst for films, liquid mixtures are first converted to solid form via drying and enwrapped the food product enclosing all sides (Upadhyay and Mishra, 2014). They don't have the properties of package wholly, but highly advantageous in barrier conditions. Both technologies discussed above are somewhat similar and their mechanism involves reducing rate of oxygen transfer along with introducing antioxidants in solutions. Considering the second technology of edible films, it finds close association with the food product. Implementation of films in foodstuffs are sustained by various attributes such as price, accessibility, thickness that provides tension, operational aspects, light transmitting properties (transparent vs. non-transparent), resistance against gaseous flow rate, sensory acceptance and impedance to microbes and moisture due to structural configuration. These attributes are controlled by circumstances that harden films (addition of solvent, increase or decrease in pH, temperature and concentration of polymers), structural formulation (molar mass and composition of material) and incorporation of additives for instance plasticizers, emulsifying and antibacterial agents (Rojas-Grau *et al.*, 2009).

The primary materials used in film structure are from proteins group, lipids and polysaccharides as summarized in Table 1. Composite compounds are formed by the amalgam of above mentioned categories. Silva *et al.* (2009) figured out the effect of synergism among several lipids, proteins and polysaccharides by combining them for the production of edible and biologically degradable films. The barrier effect and mechanical resistance in these films greatly relies on the type of components and the affinity between them (Oregel-Zamudio *et al.*, 2017). A recent technique "Smart blending" outlines the method of combining different films morphology in order to produce newly packaging materials for different foodstuffs that are able to discharge active ingredients at controlled rate. The polymers form mixtures after dispersing in water or another solvent like alcohol. Also during this process, colors, flavors, antioxidants, antibacterial or plasticizing agents are added.

Several technical aspects are being utilized for the addition of antioxidant in the films. The addition of antioxidant with plastic material is carried out via direct mixing or through extrusion method (Qin *et al.*, 2013). The incorporation of plasticizers enhanced the flexibility and extensibility of films. Under certain circumstances, the rapid release of antioxidants occurred due to higher concentration of plasticizers and increasing mobility rate of biopolymers (Gutierrez *et al.*, 2012). Tween is used with the aim of increasing emulsifying power of films. Montmorillonite, the layered silicate, is frequently utilized which in turn, reduces water vapor transmission rate and strengthen the mechanical resistance of biodegradable films (Abdollahi *et al.*, 2012).

5. Influence of antioxidant addition on characteristics of edible films

Antioxidants added in food with the purpose of delaying rancidity and their presence is strictly considered on account of some risks associated with it. Alternatively, the natural antioxidants especially plant extracts, α-tocopherol and essential oil can be used in place of synthetic antioxidants. It is also noteworthy that wastes from food industry have potential source of antioxidants. Herbs and spices have high amount of phenolic substances having high hydrogen donating activity. These are thyme, oregano, rosemary and marjoram belonging to family *Lamiaceae*, incorporated in foods for their flavor and retarding oxidation. Tea is another herb that also behaves as natural antioxidant related to family *Theaceae.* They are utilized in the form of essential oil, extract or oleoresins. The properties of films and packed food might be affected by the inclusion of substances. Hence, there is a need to check the antioxidant potential prior addition to films and coatings as well as their impact on foodstuffs and properties of wrapping material. Qian *et al.* (2014) reported that characteristics of edible films are changed by slight variations in the extract. He used murta leaf from two different species having different myricetin (flavonoid) content in it. With the incorporation of these distinct species into CMC films, their permeability to water vapor and gases had been amended.

Recently, a lot of studies have been carried out by many researchers on identifying the properties of films mechanically as well as physically and changes occurred after addition of antioxidant agents (Table 2). For instance, as reported by Pastor *et al.* (2013), the mechanical characteristics of films made by chitosan are amplified by green tea extract which proves that impact of antioxidant agents on films in a positive manner. This is due to the bonding between phenolic components of tea and amino groups of chitosan. Researches on tea extract manifested that amongst all the phenolic components, catechin is the one which is interacted with amine group in chitosan (Gomez-Estaca *et al.*, 2009). The interdependence between chitosan and phenolic components is owing to the hydrogen and covalent bonds that increase repulsion of H_2 group towards water and eventually, the tendency of chitosan film towards water is reduced. All these interactions are also observed when green tea extract is combined with the gelatin and in this way, films with less water permeability and high mechanical resistance are obtained (Li *et al.*, 2014).

Table 1. Compounds pertaining to the structural matrices of edible films and coatings

Group	Compound	Examples	Reference
Lipids	Waxes and paraffin	Bee wax, carnauba, paraffin	Singh *et al.* (2014)
Hydrocolloids	Proteins	Corn zein, gelatin, gluten, casein and whey protein isolate	Matrucci *et al.,* (2015)
	Polysaccharides	Chitosan, pectin, carrageenan, starch, alginate	Espitia *et al.,* (2012)
Composites	Several	Chitosan and gelatin, pectin and alginate, starch and sodium caseinate	Galus and Lenard (2013) Jimenez *et al.,* (2013)

Likewise, the same phenomenon was noticed in films containing polyphenol and protein components including gelatin films also. The mixture containing pomegranate peel and montmorillonite collectively improved chitosan films mechanically whereas CMC based films didn't show the same effect. The addition of citric acid also leads to reduce water vapor pressure and behave as cross linking agents (Atares *et al.*, 2011). The phenolic compounds added in protein or CHO based films are followed by two parameters: (a) their bonding or interaction with functional groups of protein and CHO that results in crosslinking (b) tendency towards water ensuing absorption of water. The influence of crosslinking has resulted in an increment in tensile strength and resistance to mechanical stress (Fabra *et al.*, 2011). However, the water vapor pressure is based on firm structure of the film and water molecules are absorbed. Consequently, it is dependent upon the amount of acid used in film causing a slight increase or decrease in it. Generally, the water vapor transmission rate is closely related to film structure (Cerqueira *et al.*, 2010). Generally, the polar substances also behave as an increment in water vapor permeability by enhancing their attraction towards water (hydrophilic).

The relative atmospheric humidity is an important factor that affects the properties of enriched films. A study by Rubilar *et al.* (2013) described the variations caused in films due to change in relative atmospheric humidity. Low humidity (35%) increased the water vapor permeability by 20% due to inclusion of extrinsic constituents such as green tea extract or quercetin in biopolymer solution. Besides these, introduction of ascorbic acid in biopolymer solution produces interaction between polymer hydroxyl groups and acid that induced extraordinary changes in barrier properties (Martins *et al.*, 2012). The absorption of green tea and quercetin in edible films kept at high humidity (90%) reduce affinity of film towards water by reducing hydrophilic attractions and barrier increment towards water. Alternatively, ascorbic acid dissolved in water due to its high tendency towards water and thereupon, resulted in films with higher water vapor permeability and elasticity. The same effects were noticed in case of oxygen permeability after the addition of ascorbic acid. It was also anticipated that insertion of antioxidant into the films caused a drop in melting point and a lack of crystallized structure (Martucci *et al.*, 2015).

Most likely, it is noticed that the antioxidant addition gives rise to two adverse conditions. It may affect the crystal of polymers by decreasing its size and increase the development of crystals to a large number (De-Dicastillo *et al.*, 2016). Carvacrol is a substance that decreases the permeability of chitosan films towards water and also tensile stress and break elongation. Gelatin based films also showed the similar phenomenon by adding carvacrol containing oil. All these consequences would result in the structural improvement of films with a reduction in elasticity, mobility and resistant to fracture when a water-repelling agent was added (Chamorro *et al.*, 2011). On the other hand, α-tocopherol is natural antioxidant having few active groups, only indicated enough increment in water vapor transmission rate instead of showing any effect on crosslinking. Also, due to its water repelling nature, it was clear that it only influenced the mechanical aspects of chitosan containing films while the oxygen permeability of whey protein films still remained same (Jimenez *et al.*, 2013).

A substance, found in grapes, called resveratrol (3,5,4-trihydroxystilbene) introduced several variations in barrier effect and ultrastructure of CMC and chitosan based films. They also cause a change in thickness of film and a reduction tensile strength but adversely as well as influenced the extensibility of films. Perhaps, the amount of substance may be increased owing to its repulsion towards water, which modified the O_2 and water vapor permeability rate to some extent (Riveros *et al.*, 2015). Some other substances such as triterpene saponins that contain plentiful amount of ginseng extract hadn't any effect on water content and water vapor permeability rate on alginate films. Despite that, it had initiated pores which caused considerable decline in modulus values such as elasticity and tensile strength. The interaction of crosslinking substances (formaldehyde) with phenolic group may interrupt the effect of crosslinking. The incorporation of anything such as fruit, herb or essential oil would leave an impact on color and transparence of coated films. The extracts of tea or fruits transmitted red or yellow color to chitosan based films and make it darker whereas green tea extract amplified the opaqueness of protein and chitosan films. Therefore, components containing anthocyanins, in addition to providing color to films also shield them against light deterioration (Akhtar *et al.*, 2012).

Table 2. Incorporation of natural antioxidants and their effects on properties of edible films

Film material	Additive	Antioxidant activity test	Influence of antioxidant on film properties	Reference
Chitosan with Tween	α-tocopherol	DPPH	Radical activity remained same when different concentrations of α-tocopherol were used.	Martins *et al.,* (2012)
Gelatin with propylene glycol	Oregano and lavender essential oils	ABTS	Antioxidant properties are highly effective in oregano based films.	Matrucci *et al.,* (2015)
Chitosan with glycerol	Green tea extract	DPPH, total phenolic content	Increasing green tea concentration has increased TPC and DPPH scavenging activity	Galus and Lenard (2013)
Alginate with glycerol	Extracts of white (WG) and red ginseng (RG) ethanol	FRAP, DPPH	Antioxidant potential can be amplified by addition of these extracts. RG has higher DPPH scavenging activity than WG.	Norajit *et al.,* (2010)
Chitosan-MMT nanocomposite with Tween	Rosemary essential oil	TPC	TPC increased but WVP decreased with the increasing concentration of EO	Abdollahi *et al.,* (2012)
Corn starch-sodium caseinate and glycerol	α-tocopherol and oleic acid	ABTS	Addition of tocopherols enhanced the antioxidant potency of films whereas it was reduced by oleic acid.	Jimenez *et al.,* (2013)
Cellulose acetate with triethyl citrate	Acetone, onion ethanol or water extracts	ABTS, TPC, DPPH	Absolute ethanol extracts and 85% ethanol in water had the highest antioxidant potential.	Dicastillo *et al.,* (2016)
CMC with glycerol and Tween	Clove essential oil	DPPH, TPC	Increasing oil concentration resulted in increased antioxidant potential.	Gutierrez *et al.,* (2012)

6. Integration of various components into mixtures of edible films

Different constituents for instance emulsifying, anti-browning, antioxidant and antimicrobial agents, colors, spices, plasticizers, surface active agents, nutrients, textural modifiers are also added into the films (Kang *et al.*, 2013). The purpose of their addition into films is to modify poor mechanical and barrier attributes of edible films *e.g.* tensile force and augmented its use in different food applications. Limited barrier effect in films due to hydrocolloids (hydrophilic substances) can be enhanced by the insertion of lipids as they are good water repelling agents and resistant to water content (Alves *et al.*, 2011).

6.1. Plasticizing agents

They are defined as constituents having lower molecular mass; incorporated into the solid films with an aim to improve film firmness and strength, imparting elasticity and modify its flow rate by reducing brittleness (Hamzah *et al.*, 2013). As related to edible films and coatings, the functional role of plasticizing agents is the enhancement in film strength and flexibility by reducing flaking and cracking in films. The major drawback of using these plasticizers is the increment in permeability of film to water, O_2, aroma and oils owing to decrease in attractions between molecules. They are usually utilized in the films composed of protein or polysaccharides and their dependence basically relies on following parameters: high polar charge, smaller size, location of polar groups in molecule and distance between them and number of polar groups/molecule. These characteristics play an important role in biopolymer matrix. The carbohydrate polymers such as monosaccharides (glucose), disaccharides (sucrose) and oligosaccharides (high fructose corn syrup, honey) are common examples of plasticizing agents commonly used in biodegradable films (Galus and Lenart, 2013). Also, lipids and its derived products such as waxes, phospholipids, surface active agents and polyols (sorbitol, glycerol and polyethylene glycol) are also used. Water would serve as a plasticizing agent as it breaks the hydrogen bonds in hydrophilic system.

6.2. Antioxidant agents

Lipids have the function to decrease the water vapor transmission rate in biodegradable films due to their property of being hydrophobic. Therefore, antioxidants are added in order to protect them from rancidity, decolorization, and deterioration and extending shelf life of food products. It was also suggested by scientists that some antimicrobial substances also possess antioxidant characteristics (Grosso *et al.*, 2020). Synthetic antioxidants are also in use now-a-days along with natural antioxidants. As it is mentioned earlier, some compounds such as vitamin C and E, citric acid, oregano and rosemary extracts, ferulic acid and phenolic components are mostly utilized as antimicrobial agents.

Xiao *et al.* (2012) reported the antioxidant potential of materials used in film such as extracts from brown seaweed (*Laminaria digitata* and *Ascophyllum nodosum*). The comparison of two species showed that later had more antioxidant potential as former. The results revealed by Rojas-Grau *et al.* (2009) also showed the antioxidant effect on bream (*Megalobrama amblycephala*) quality by incorporating ascorbic acid and polyphenolic tea components in alginate solutions. A big difference in quality and storage life was found in uncoated breams with respect to bream coated with tea and ascorbic acid. Thereupon, the ascorbic acid maximizes its use in edible coatings by preventing moisture loss, maintaining sensory quality, retaining nutritional value and delaying rancidity.

6.3. Anti-browning agents

The functional perspective of these substances is the inhibition of enzymatic browning in cut foods like fruits and vegetables and extend their shelf life. The addition of these agents in edible films and coatings has led to an improvement in color and leave a positive impact in food preservation. Many compounds such as citric and ascorbic acid, methionine and cysteine can act as anti-browning agents and are incorporated in films solutions to avoid enzymes induced browning in foods. The capability of alginate coatings to incorporate anti-browning compounds (cysteine and methionine) and was performed by Kafrani *et al.* (2016) who examined the anti-browning effect in retarding water loss in cut apples. The results expressed that both showed their effects on cut apples. The former anti-browning agent exerted influence in a positive manner whereas the glutathione effect was negative. Additionally, citric acid and ascorbic acid act as anti-browning agents by prolonging shelf life and ensuring food quality.

6.4. Antimicrobial agents

Edible films and coatings coupled with antimicrobial substances serve as an inhibitor in reducing microbial population and weaken the growth spoilage microorganisms (Azarakhsh *et al.*, 2014). The utilization of chemically antimicrobial substances *viz* potassium sorbate, ascorbic and propionic acid has some limitations in its consumption owing to issues related to health. Thus, GRAS (generally recognized as safe) recognized compounds are demanded by consumers from health point of view. Sometimes, the naturally produced antimicrobials or enzymes *e.g.* lysozyme and nisin are used as preservatives during packaging process. In addition, the by-products of plants such as extracts or phytoalexins, chitosan and organic mixtures (malic, citric, and lactic) are also used as antimicrobials. The use of these compounds as active packaging in edible films is of great importance.

Metal based nano-particles are extensively used now-a-days as antimicrobial agents by degenerating cell membrane and lead to cell death (Osorio *et al.*, 2011). Using nano-technology, silver has proved to be actively used as an antimicrobial agent. It causes the interruption in bacterial growth by entering into cell and disrupting cell membrane. The impact of nano-silver with alginates on mushroom quality was carried out by Jiang *et al.* (2013) who studied the variations occurred in mushrooms throughout the storage. The conclusion was that the coating was effective in retaining the quality of mushroom and subsequently, can be used in preserving them for long time. It was also reported that marjoram was more effective in retarding microbial growth as compared to clove and cinnamon extracts when films having nano-materials/alginate were analyzed. The combination of biopolymers especially guar gum, gelatin, pectin and starch with antimicrobials such as nisin, Guardian NR100, Novagard CB 1, sorbates, lactates and acetate compounds with the purpose of controlling microbial spoilage in turkey products (Pascual *et al.*, 2014). Of all the above biopolymers, alginate antimicrobial coatings promoted microbial safety and product quality by preventing *Listeria monocytogenes*. Also, blend of nisin with lactate resulted in prolonging the shelf life of carrots.

6.5. Other agents

Probiotics, prebiotics, vitamins (water soluble and fat soluble) and minerals (major and minor) are also added in films and coatings in order to amplify their functional roles. Biodegradable films and coatings also serve as a medium to deliver beneficial nutrients and nutraceutical substances in the foods that usually contain less amount (Kowalczyk and Baraniak, 2011). Besides these, color containing pigments and flavoring compounds are also used as extra additional substances in films and coatings with an advantage of modifying sensory characteristics of food products.

6.6. Pragmatic gains and notorious outcomes

As discussed above, there are no lethal effects of edible films and coatings in ecological system. For instance, the carrageenan has some positive impacts such as immune modulator, anticancer, anticoagulant and antithrombotic activity. Likewise, it also has higher antioxidant potential as in ƛ–carrageenan. Regardless of that, carrageenan also has adverse effects relevant to carrageenan having molecular mass less than 50kDa (Alboofetileh *et al.*, 2014). This type of carrageenan has resulted in intestine inflammation. The effects of all carrageenan (ƛ, ƙ) were also reported and lambda carrageenan had the highest and kappa was seen to have lowest inflammatory activity. It was proved by analysis that there was direct relation between sulfate groups and increase in sulfates led to an increase in carrageenan activity.

Though, carrageenan appears to be toxic at high dosage that have no relation with food additive. So, it is important that carrageenan should have molecular mass more than 100,000Da. Contrary to carrageenan, the authors also described the benefits of alginate as film material. Instead, it is also noteworthy that presence of foreign matter like proteins, phenolic components, metals (mercury, cadmium, arsenic etc.) and endotoxins in alginates show immunogenicity (Hambleton *et al.*, 2012). On the other hand, pure alginates with no extraneous matter have no immunogenicity. The group of alginates are called as dietary fiber and its beneficial impact on colon and intestine are also reported. The utilization of alginate as medicine has also demonstrated. This is due to the potential of alginates that produces cytokines having high mannuronate content in contrast to alginates having high guluronate residues (Houghton *et al.*, 2015).

7. Need of microencapsulation

Natural oxidants have a tendency to be easily oxidized and response sensitivity towards heat and light (Chao *et al.*, 2012) which minimize their consumption in food industries. These substances are not directly added to foods due to some distinctive limitations on account of less accessibility, undesirable flavor, and highly sensitive to processing, environmental as well as gastric conditions. Amongst the prevailing stabilization methods, microencapsulation is a strategy to resolve all these issues sustaining their stability, increase bioavailability and retention time in food matrix and masking their aroma and delay onset of oxidation and hydrolysis under processing conditions while maintaining their functionality (Aguiar *et al.*, 2016). It has miscellaneous applications in the field of pharmaceutical, cosmetics and agrochemicals.

Active food packaging has opened the doors of food preservation. Here is the technique "microencapsulation" that includes the protection of active ingredients (central material) from environmental harsh conditions by a layer of encapsulating material. So, the encapsulating material may be called as the wall material while the central material (active ingredient) forms the core. This technique is used to make edible films from food material which form microcapsules in the range of micro or nano. This process behaves as hindrance and keep the sensitive ingredients safe from external environment from adverse conditions such as oxygen, moisture and temperature (Ozkan *et al.*, 2019). Antioxidant therapy is a potent tool to lessen stress induced by oxidation in body since they have ability to delay reaction initiated through free radical scavengers. Our diet also cover foods such as fruits, vegetables, edible mushrooms that contain some amount of natural antioxidants (Oroian and Escriche, 2015).

Under the storage conditions, bioactive compounds such as BHT loses its physical and chemical properties due to its sensitivity after exposure to environmental conditions. There is an optimal need of encapsulation in order to prevent interaction of these compounds with water, oxygen and other environmental factors that cause degradation (Santos and Meireles, 2013). The purpose to infuse antioxidants during film formation is followed with the fact that its movement in unrefined foods or food simulators is described in terms of their release rate at target points. Structural properties may have an impact on rate and amount of active agents involved in transfer and mechanical and barrier properties affect polymer stability in different conditions (Jamshidian *et al.*, 2012). Oxidation yields low molecular size off-flavor complexes that diminishes vital nutrients and yields lethal substances and polymers or dimers of proteins and fat. As free radicals were counted as the cause of oxidation, thousands of compounds have been introduced to lower the efficacy of radical scavengers or in case to reduce their inhibitory properties. Mostly, these four antioxidant agents have been extensively used in foods named as BHA, BHT, TBHQ and PG (propyl gallate).

8. Film forming materials

Single polymers as gelatin, pectin, alginate, chitosan, guar gum and derivatives of cellulose are employed in case of simple coacervation in contrast to combination of biopolymers as pectin/gelatin, gelatin/guar-gum, alginate/CMC, pectin/gum arabic, gelatin/gum arabic and glucan/carboxymethyl cellulose in complex coacervation (Zuanon *et al.*, 2013). Among them, gelatin/gum arabic is the best combination in terms of their charges and labelled gelatin and gum arabic as positive and negative electrolytes respectively. This process is used extensively to encapsulate fat-soluble (hydrophobic) substances as for example α–tocopherols, naturally occurring carotenoids (lycopene, β-carotenes, and lutein) and palm oil. Also it is applicable to encapsulate large number of water soluble materials (Rutz *et al.*, 2016). The description of some of the film forming materials was described below:

8.1. Cellulose

Of all the organic compounds, cellulose is abundantly found in nature. It is a straight chain biopolymer consisting of glucose units joined together through β-1,4-glycosidic bonds. It is insoluble in water and non-digestible owing to absence of cellulase enzyme in humans although it behaves as a dietary fiber. The derivatives of cellulose such as carboxymethyl cellulose (CMC), methylcellulose (MC) and hydroxypropyl methylcellulose (HPMC) have the ability to form biodegraded, colorless edible films. It is also reported that CMC has property of gelatinization upon heat and water solubility which makes it effective during film formation. As far as its hydrophilic property is concerned, cellulose based films show poor barrier properties against water (Realini and Marcos, 2014).

8.2. Pectin

It is a complex anionic polysaccharide, naturally found in apple and citrus peel and consists of long chains of α-1,4 linked galacturonic acids. It is used as thickener, stabilizer in dairy products as ice-cream, yogurt and as gelling agent in marmalades, jellies and jams (Giancone *et al.*, 2011). They are applicable for use in edible films and in food industries. The application of pectin as film material has an excellent degree of resistance to oil, aroma and O_2 and limited barrier against moisture, low extensibility rate, and higher elastic modulus. The addition of plasticizer has reduced their brittleness and provided flexibility. The addition of Ca^{+2} (multivalent cation) into films would promote crosslinking and bring about a change in mechanical characteristics (Espitia *et al.*, 2014). Another prime function of pectin is that it acts as a humectant, as gel holds water and protect foods from spoilage. Due to this property, they can be used as packaging material for vegetables (tomato, raddish, cabbage) and fruits (apricot, apple, guava and berry).

8.3. Starch

Unlike cellulose, starch is a branched chain polysaccharide and consists of glucose monomers joined together through α-1→4 linkages. It provides firm structure to edible films and produces semi-transparent, odorless, tasteless and colorless films. It occurs in the form of granules and become soluble when dissolved in hot water. Upon heating, it absorbs water having hydroxyl group as side chains and swells. The semi-crystalline structure of granules is lost, it absorbs more water and viscosity increases until it reached the critical point. It is the point at which specific amount of starch is required to make a gel at 95°C (Sucheta *et al.*, 2019).

8.4. Guar gum

It is extracted from the guar plant (*Cyamopsis tetragonoloba*), also known as guaran, has a number of applications in foods and in industries. Its structural backbone mainly consists of β-1,4 mannose linked to 1,6 galactose units, as galactose form the side chains and mannose residing inside (Banegas *et al.*, 2012). As it is water soluble, it is suitable for film formation owing to property of higher molecular mass and long polymeric chains. Besides, they have poor barrier properties due to which their use in edible films is limited. In food applications, it is utilized as a stabilizing, thickening and emulsifying agent. Nutritionally, it delays the satiety time and acts as a laxative in treating constipation and diarrhea (Das *et al.*, 2011).

8.5. Alginates

It is extracted from brown seaweed belonging to family *Phaeophyceae* linked α-1→4 linear unbranched chains. Its structure has three blocks such as M, G and MG block containing residues of α–L-guluronic acid and β–D-mannuronic acids at different concentrations (Erginkaya *et al.*, 2014), depending upon the origin and age of plant. The alginate films have a high degree of food quality and significant increase in moisture barrier, retaining sensory characteristics and delaying lipids oxidation. The presence of Ca^{+2} ions improve their water vapor permeability and form strong or insoluble gel when interacting with multivalent ions. Modernized food products such as onion rings and cocktail berries also considering this type of gel. However, reaction of alginate with calcium cations is so fast that it can inhibit film formation (Ramos *et al.*, 2012).

8.6. Arabic gum

It is extracted from several species of *Acacia* plant and also known as "acacia gum". It is water-soluble and not digested by humans and animals. Its composition mainly consists of d-galactose, d-glucuronic acid, l-rhamnose and l-arabinose. It is widely used in food industry as it has unique properties of emulsifying, encapsulating and biofilm formation (Ali *et al.*, 2013). It is used as a stabilizer, thickener, emulsifier in confectionary as in soft candy, icing, chewing gum and in baking products. It also finds its use in packing of fruits and vegetables such that the gum arabic coating revealed a substantial decrease in ethylene production and cellular respiration (Mahfoudhi and Hamdi, 2014).

8.7. Agar

It is a gelatinous substance obtained from red purple algae, belonging to family *Agarophytes*, also called "agar-agar". It is mainly composed of agarose and agaropectin: agarose has repeating units of agarabiose and agaropectin has a mixture of D-galactose and L-galactose units. Its important feature is that it makes gel at low concentration and less viscous solutions. It is generally used in food industry to make puddings, jellies and custards (Phan *et al.*, 2005).

8.8. Carrageenan

A marine sulfated polysaccharide, food additive, extracted from red seaweed (Irish moss) belongs to *Rhodophyceae* family. Carrageenan occurs in three forms: kappa, iota and lambda carrageenan forming different types of gels at different temperatures. The kappa, iota and lambda carrageenan have one, two and three sulfate groups per disaccharide respectively (Karbowiak *et al.*, 2006). They are basically used in dairy and meat industry as stabilizer, thickener and emulsifying agent. The application of carrageenan in edible films in enhancing water barrier provides strong basis for meat, fish, sausage casings, fatty foods, and poultry foods. Due to helical structure of carrageenan, it is reported that the film formation involves the gelation mechanism at room temperature, which leads to solid stable films after evaporation of solvent.

8.9. Chitin and chitosan

Chitin is abundantly found in nature after cellulose. It is the primary component of animal cell wall as fungi in exoskeleton of crustaceans such as shellfish, lobsters and prawns in scales of fish and other living organisms (Danalache *et al.*, 2016). Another cationic polysaccharide, chitosan, produced as a result of deacetylation of chitin, having higher molecular mass and significant potential of film formation and antimicrobial effect. When chitosan film is mixed with another biopolymer, it has been employed for packaging of variety of foods that provides extraordinary protection over a wide range. It has been used in making gels, fabrics, sponges or nanoparticles. In light of positive attributes such as biodegradable, toxic-free and biologically compatible, the chitosan films retain freshness of fruit by delaying enzymatic browning, control cellular respiration and the oxygen pressure in package and maintain temperature between food and its surroundings (Nayik *et al.*, 2015).

8.10. Xanthan gum

It is an exopolysaccharide, produced during fermentation of sugars from bacterium *Xanthomonas campestris.* It acts as a stabilizer and thickener but not as emulsifier. It only prevents solutions from separating and thus, regarded as safe material (Jain *et al.*, 2016). It can used at the concentration of 0.5-1.0% to make a significant increase in viscosity at specific temperature and prevent enzymatic deterioration. Xanthan gum finds its use as coatings in extending life of fresh-cut fruits, as well as releasing bioactive compounds encapsulated in films to target points. Similarly, the addition of acerola fruit with xanthan gum would retard ripening process in fruits. Its structure primarily consists of β–D-glucose units with two mannose and one glucoronic acid as side chains.

8.11. Gelatin

Collagen films are mostly utilized in meat industry for meat processing and its preservation as they maintain humidity and provide uniform characteristics to food product. Collagen is naturally found in animal bones, muscle, skin, and connective tissue and undergo alkaline/acidic treatment at 40°C, which gives gelatin (Hanani *et al.*, 2014). The produced gelatin readily dissolves in hot water and gel when cooled. With the purpose of making edible films from gelatin, it is immersed in hot water and then casted on a plate to form layer and then dried. The thickness of films depend upon the protein content, showing an increase in mechanical characteristics with a decrease in water vapor barrier. Additionally, gelatin films also illustrate antimicrobial and antioxidant characteristics. Antioxidant potential is measured by DPPH radical scavenging activity (%) and antimicrobial activity is evaluated by disc diffusion method as shown in Table 3. Disc diffusion technique refers to clear zone around a film disc and no clear zone indicates no inhibition. For better antimicrobial effects, the concentration of functionalized ingredients in film solution should be above minimum inhibitory concentration (MIC).

8.12. Milk protein

The proteins found in milk are also used to make films as well as a colorant, antioxidant and antimicrobial agent. Casein protein make up the 80% of cow's milk and include four types of protein: αS1, αS2, β, and κ. Casein is obtained by skimming of milk at 21°C and separate caseinate compounds by alkali treatment. The separated casein is then washed, pH is increased to 7 by adding alkali ($Ca(OH)_2$ and NaOH) and then dried. The polyvalent Ca^{+2} cations increase crosslinking interactions between proteins. Sodium caseinate films have excellent optical and mechanical properties whereas films of calcium caseinate have improved barrier effect. All such type of films have good oxygen resistance but poor water barrier effect (Wagh *et al.*, 2014). The remaining aqueous portion left after casein precipitation is called whey, in which α–Lactalbumin, β-Lactoglobulin, immunoglobulins and serum albumin are dispersed. Whey protein isolate (WHI) covers 90% of whey protein that is used as film-forming material. In past, whey protein concentrate is used for films as it contains extraneous substances that resulted in poor tensile properties. WHI is much better than calcium caseinate and whey protein concentrate as it replaces 50% calcium caseinate in films without diminishing puncture strength (Oses *et al.*, 2009).

8.13. Zein

It is the prolamine protein, extracted from maize/corn having hydrophobic and plastic like characteristics. Zein proteins are transparent, hard, colorless, and insoluble in water and serve as a carrier as antimicrobial and antioxidant agent when utilized in edible films (Estevinho *et al.*, 2016).

Table 3. Effect of functional ingredients on antioxidant and antimicrobial aspects of various types of gelatin films

		Antioxidant	Antimicrobial		References
Type of film	**Ingredients**	**DPPH (%)**	**Microbes**	**Test**	
Fish gelatin	Mango peel extract	73.0-84.5	------	------	Matrucci *et al.,* (2015)
Fish gelatin	Peel extract of *Punica granatum*	59.0-71.6	*S. aureus and E. coli*	Disc diffusion	Hanani *et al.,* (2014)
Bovine gelatin	*Centella asiatica* extract	34.6-47.4	------	------	Li *et al.,* (2014)
Gelatin	Tannic acid	-------	*S. aureus and E. coli*	Disc diffusion	Zuanon *et al.,* (2013)

8.14. Soy protein

It is the soybean protein and occurs in different forms as soy concentrate, soy flour and soy protein isolate (SPI) having 66%, 55% and 90% protein respectively. Soy protein isolate is mainly used in film production and the presence of foreign substances except SPI have negative influence on film properties. They are transparent, shiny and elastic texture and are considered important in terms of barrier properties. Although, they show good oxygen resistance, but their ability is 260 times less as compared to starch and pectin films (Reesha *et al.*, 2015).

9. Methods of encapsulation

There are three types of techniques such as physical, chemical and physicochemical methods. Some of the physical and chemical methods are spray drying, lyophilization, interfacial polymerization, solvent evaporation and supercritical fluids (Tyagi *et al.*, 2011). The target of present review is to describe physicochemical techniques utilizing complex coacervation.

9.1. Microencapsulation through complex coacervation

In physicochemical, a sequence of colloidal phenomena that include aqueous phase separation of solo or a merger of two complementary charged biopolymers is called coacervation. Coacervation encompasses four distinct classes of interactions namely hydrogen bonding, polarization, electrostatic interactions and hydrophobic bridges (Poncelet, 2006). Polarization is liable to attractions as well as induce enzymatic or chemical agents together with glutaraldehyde or transglutaminase. The intensity of interactions among the biopolymers can be computed considering a number of factors for instance type of polymer (molecular weight, degree of flexibility and corresponding charge), ionic strength, pH, ratio of the biopolymers and concentration. Coacervation is primarily used for encapsulation of antioxidants, β-carotene, turmeric and lycopene (Qv *et al.*, 2011). Course of coacervation might be simple or it might hold some complexities which are essentially dependent on the quantity of polymers utilized. At one hand where simple type of coacervation encompasses only a single polymer in amalgamation with solid water loving agents and a colloidal mix, complex type coacervation is manufactured via mix up of two or even additional polymers for wall foundation round a dynamic core.

The key benefit of complex type coacervation is the fabrication of microcapsules which are of smaller dimensions which mainly range from about 1-1000 µm (Zuanon *et al.*, 2013). Briefly, complex type of coacervation is supported firstly via development of an emulsion that is dispersed into a liquefied polymeric mixture. At that point, it is being followed by wrap up of the phase that is an even layering round the cored material by the addition of a second watery mixture endorsed by the fortification of salt, thus fluctuating pH, temperature of the aforesaid mix and dilution of the same medium (Lupo *et al.*, 2014). The solvable, accumulated or the precipitated complexes are mainly attained prior filtration or the process of centrifugation is executed to acquire aforementioned microcapsules, proceeded by a brief step of washing using proper solvent and finally the drying step.

According to the statement of Arfat *et al.* (2017), while preparing the formulations for micro-encapsulation via emulsification procedure, firstly core is immersed into an organic solvent exactly where the wall material lies. Afterwards, immersion is kept in the water or oil to accomplish emulsification which comprised of the emulsion stabilizer. Organic solvent is thereby detached via evaporation stimulated by stirring, thus providing formation of dense polymeric globules within which core is encapsulated (Diaz *et al.*, 2015). This method has been repeatedly utilized as a result of the ease of operation associated with the production of particles and also the type of the constituents of aforesaid formulation and more importantly the preparatory conditions. Emulsification is being practiced for the encapsulation of vitamins, probiotics, enzymes, and minerals. By utilizing microencapsulated enzymes via emulsification in making cheese, there was an aggravation in the rate of protein degradation as compared to those of free enzymes. The microencapsulation of some strains of probiotics by Badawy and Rabea (2018), employing the technique of emulsification using alginate-chitosan as polymeric system, representing enhanced confrontation against gastric conditions.

Lyophilization is defined as technique comprising of the water withholding freeze matrices with the help of vacuum sublimation, whereas composite water exclusion takes place not submitting samples to elevated temperature. This mode offers outstanding quality products. The reason is it diminishes the deviations owing to high temperature, it is extensively manipulated in flavorings. However, the high initial cost and also the long processing time emasculate its large scale applicability. Song *et al.* (2011) was the one to microencapsulate virgin oil of olives while in the presence of maltodextrin, carboxymethyl cellulose and lecithin by the process of lyophilization, depicting that the oil was very much the same after for 10 months, which improved its keeping quality. Pinzon *et al.* (2018) encapsulated extract of garcinia fruit in whey protein isolates and maltodextrin by the process of lyophilization and applied in bread that demonstrated elevated volume, soft crumb texture, appreciable color and commendable sensorial attributes.

Impacts of coacervation procedure mostly on food grade antioxidants have been reviewed in a few researches. A study reported by Jain *et al.* (2016) investigated the creation of micro-encapsulated formulation of β-carotenes via complex coacervation procedure manipulating the indigenous protein of dairy origin casein and tragacanth gum as subsequent wall matrix. Antioxidant propensity of the free β-carotenes and frozen dry form of carotene filled microcapsules were mapped with the help of 2,2-diphenyl-1-picrylhydrazyl (DPPH) method up to a span of 90 days for inspecting the influence of encapsulation procedure and matrices i.e. of β-carotene (Singh *et al.*, 2014). Results pertaining to this indicated that there was an obvious fluctuation on the completion of 3 months in the % scavenging activity of the free β-carotenes. Frozen dry β-carotene filled microcapsules represented that extended steadiness of β-carotene was mainly functionalized inside the complex micro-capsular matrix. Likewise, the similar research was carried out to study the possible procedures to overwhelm limited water solubilization and low stability characteristics of β-carotene by the process of complex coacervation employing another milk protein whey which is isolated and gum procured from acacia tree. Therefore, they assessed microcapsules considering percent scavenging activity (Xiao *et al.*, 2014).

The technique of coacervation is primarily considered superior to conventional techniques of microencapsulation owing to its considerably low temperature, capacity to carry high loads, and lessened losses from evaporation or degradation by heat and alliance to govern the control release of active material from them (Taneja and Singh, 2012). Likewise, a particular instrumentation is not obligatory for its employment and it also has got simple formulating conditions for instance utilizing toxic-free solvents as well as low utilization of agitation (Ballesteros *et al.*, 2017). Conversely, an elevated cost of isolation of particles and complexity associated with the technique ought to be taken under consideration.

Morphological specification of microcapsules developed employing this sort of technology is either mono-nucleated or poly-nucleated. The morphology of cells includes the formation of emulsion and depends upon the type of biopolymers, ratio and its concentration, molecular mass and corresponding charges (Gharsallaoui *et al.*, 2007). In addition to these, some other factors such as temperature, solidifying as well as cooling rate and its pH also affect the internal structure of cells. All these factors are interlinked with each other and make this process an optimizing one.

10. Characteristics of microcapsules

10.1. Structural characteristics

Both simple and complex processes require protein with appropriate amino acid content and charge carriers. For instance, the polymer gelatin has corresponding charge and amino acid arrangement such as the repeated units of proline and hydroxyproline in glycine-X-Y- triplets representing X and Y as glycine and hydroxyproline respectively (Kaushik *et al.*, 2015). Regardless of an anion, the helical configuration of gelatin keeps an adequate charge in order to prevent deposition of gelatin chains. In the same way, the similar pattern was observed in gum-arabic preventing precipitation of its chains by blocking water. This type of helical structure proves to be useful in formation of microcapsules as charge carriers and increases the chances of interaction to a large extent.

10.2. Rheological characteristics

For the generation of microcapsules, the interlinking between polysaccharides and proteins is considered substantial. It is also reported that the mixing of polymers completely neutralizes the polymer charges which in turn, brings about an optimal increase in viscosity. Thus, the stability of microcapsules depends upon the viscosity of coacervates. The following mentioned factors greatly influence the rheological characteristics, such as corresponding charge carrier, molecular mass and structural configuration as well as ongoing process conditions, including pH value, concentration of ions in solution, temperature and proportion of protein/polysaccharide. The size of micro-particles produced is also differed by polymers as well as matrix viscosity (Fai *et al.*, 2016).

Conclusion

Natural antioxidants represent best additives for edible films and coatings considering the aspect that they increased the phenolic content and scavenging activity as well as modifying the barrier properties through interactions with the active groups. The mechanical characteristics of films are affected by presence of natural ingredients (flavonoids, phenolic acids, etc.) and the distribution of the additive in the polymer matrix, therefore, they should be examined carefully. Another key factor that requires attention is the stability of the antioxidants is their release rate throughout the storage of the packaged food and its impact on organoleptic traits of food product. These factors decide their application in food industry. Utilization of natural antioxidants in active packaging may lead to innovative solutions with an aim to retain quality and in prolonging the shelf life of food products.

Authors contributions.

All the authors listed in this manuscript contributed and approved the manuscript.

Conflict of Interest

Authors listed in the manuscript have no contending interest.

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