

REVIEW ARTICLE

Recent advances in active packaging of agri-food products: a review

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ABSTRACT

Food products are vulnerable to biochemical spoilages and microbiological contamination through light, water vapour, oxygen and other outside environmental barriers, in spite of the upcoming barrier film technologies, preservation techniques and processing methods. Thus, there is a need for appropriate packaging technology to increase their shelf-life. Active packaging is increasingly becoming popular that can prove to be an indispensable vehicle in the preservation of food items as it provides barrier to external influences as well as preventing contamination inside the package. Active packaging can be defined as the inclusion of an active system into packaging film or a container to maintain the quality or extend the shelf life of the product. Major active packaging systems such as moisture controllers, oxygen scavengers, carbon dioxide emitters/absorbers, antioxidants, ethylene absorbers, flavor releasing/absorbing systems, antimicrobials etc. have been discussed and their mechanism of action along with their effect on the shelf life of foods has been briefly outlined in this article. Efforts have been made to review the past as well as recent researches along with its future perspectives through this article, w.r.t active packaging as an upcoming and novel preservation and packaging technique. Developments in nanotechnology will also enable the advances for a better and novel active and intelligent packaging.

Keywords: Active Packaging, O₂, CO₂ emitters/scavengers, moisture absorbers, antioxidants, antimicrobials

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INTRODUCTION

The type of packaging plays an important role in determining the shelf life of food products. A good packaging system is expected to protect the food from the contaminants and factors that limit its shelf life. A packaging system must be inert, prevent entry of microorganisms, non-toxic, stable and also protect food from the aspects which deteriorate food quality during transporting and handling (Sung, 2013). Active packaging system has the potential to offer significant advantages in preventing quality loss in horticultural products by controlling the physiological activity and extending the shelf life of food products. According to Dainelli et al. (2008), it can be classified as non-migratory active packaging that elicits a response without migration of the active compound into the food (oxygen absorbers are an example of these systems), most of them are based on iron oxidation, but they can also be based on ascorbic acid oxidation, catechol oxidation or enzymatic catalysis. By

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delivering and sustaining volatile active agents at effective levels in a package atmosphere, significant shelf life can thus be achieved. Passive packaging has been used in an effort to minimise the deleterious effects of a limited number of external variables such as oxygen, water, light, dust microorganisms, rodents and to some extent, heat. Hence, active packaging rectifies the loopholes and deficiencies that exist in passive packaging. Active packaging is typically found in two types of systems: specific active ingredients that are incorporated directly into the packaging polymer-based films or coatings, and sachets and pads in which specific additives are placed within the container itself (Liang and Ludescher 2011). Active packaging, in which active agents are embedded into or on the surface of food packaging materials, can enhance the nutritive value, economic value, and stability of food, as well as enable in-package processing (Wong and Goddard 2014).

Before applying any system of active packaging, the mechanism by which foods deteriorate needs to be understood in order to increase their shelf life. Fruits and vegetables, either fresh or minimally processed, are very much prone to pathogenic spoilage and undergo unsolicited biochemical changes during transportation and storage. Scientific investigations have proved that an increased consumption of fruits and vegetables is known to reduce instances of cancer and cardiovascular mortality (Bhardwaj et al., 2014). Over the past 10 years, there has been a great elevation in the demand for value added food products. Thus, there is a need for preservation and prevention of spoilage of these commodities. The fresh food utilizes the oxygen in the headspace of the package and increases the carbon dioxide concentration. When one part of the package becomes cooler than the other, water vapour condense as droplets of liquid and the humidity in the headspace of the package increases which encourages the growth of ubiquitous mold spores. Similarly, flesh foods such as meat, poultry, fish are vulnerable to rapid microbial spoilage due to high water content and optimum pH, which contribute to the proliferation of the spoilage microbes. Various types of food products such as minimally processed and non-processed foods such as seafoods, fresh agricultural produce or seasoned produce whose distribution requirement over large distance is respiration. If these respiration requirements are met under controlled atmosphere conditions then these products shelf lives will be extended for a longer period of time. Thus, it is needed to solve the problem for storage and long-distance shipping as well as enhancing the final product quality. Milk and dairy products such as cheese, yoghurt etc. gets easily spoiled by microorganisms due to their high-water activity. Nevertheless, the concept of integrating microbiostatic and microbicidal materials and plastic packaging has been very attractive. Numerous attempts have been and are being made to translate favourable laboratory results into safe and effective commercial food packaging. The food packaging community has been experiencing many accomplishments in the active packaging arena including oxygen scavengers, CO₂ emitters etc. Thus, active packaging systems with oxygen scavengers, CO₂ emitters, dessicants, antimicrobial compounds, antioxidants etc. provide an innovative packaging technique to extend the shelf life of food products by incorporating certain additives, either into the packaging films or inside the headspace of the food package along with increasing food safety, reducing the use of food additives, decreasing food loss and developing new products.

The active packaging systems and their mechanisms along with their respective applications have been listed in Table 1. New concepts of active packaging, intelligent packaging and nanotechnology offers innovative solutions which plays an important role for improving or monitoring food quality & safety and extending shelf-life (Dobrucka and Cierpiszewski, 2014). This article shall be reviewing the past as well as recent researches along with its future perspectives, w.r.t active packaging as an upcoming and novel preservation and packaging technique. Some applications for active packaging technologies and their effect on foods are summarized in Table 1.

Table 1: Selected examples of active packaging systems

Active packaging systems	Food applications	References
Oxygen scavengers	Increases shelf life of Cheese Spread Increase the shelf life in cakes Quality improvement and increase the shelf life in dark chocolates Inhibition of ascorbic acid degradation in beverages	Gomes et al. 2009 Guynot et al. 2003 Mexis et al. 2010 Baiano et al 2004
Carbon dioxide scavengers/emitters	Packaging nuts and sponge cakes.	Rooney, 1995
Ethylene scavengers	Reducing the rate of softening in tomatoes	Bailen et al. 2006
Odor releaser and antimicrobial	Quality improvement and antimicrobial activity in roast beef	Gutierrez et al. 2009
Ethanol emitters	Extending microbial shelf life of rye bread Shelf life extension of pre-baked buns.	Salminen et al., 1996 Franke et al, 2002
Antioxidants	Quality improvement of apple slices Quality improvement in milk powder	de Oliveira et al. 2008 Granda-Restrepo et al. 2009
Antimicrobial	Increase the shelf life in fresh beef Antimicrobial activity against filamentous fungi and yeast in butter Inhibition of <i>L. monocytogenes</i> in cooked ham Extension of shelf life of bread Antimicrobial activity against Lactobacillus acidophilus, Pseudomonas fluorescens, Listeria innocua, and Escherichia coli in Raw fish products and salmon Increase the shelf life in grilled pork Antimicrobial activity against Rhizopusstolonifer in Sliced bread Inhibitory effect of selected oils and oleoresins against molds and yeast associated with bread	Zinoviadou et al. 2010 Moraes et al. 2007 Jofre et al., 2007 Jideani et al., 2013 Gomez-Estaca et al. 2009 Yingyuad et al. 2006 Rodríguez et al. 2008 Nielson and Rios 2000
Odor controller	Extending the shelf life of fillets of sole, steaks of cod, and whole cuttle fish	Franzetti et al. 2001

FACTORS IMPORTANT FOR ACTIVE PACKAGING

The active packaging should realize conditions that are mentioned below:

- The active packaging material should include manufacturing of the material in accordance with its correct code of conduct (Good manufacturing practices). Also, it must be appropriate and effective for its intended use.
- The material must display correct information about the active ingredients added or particles that may be released by the active component inside the package. Complete information about their name, amounts and other specifications must be present on the package.
- Warning label “DO NOT CONSUME” should be observable, comprehensible, indelible and clearly written in bolds, so as to allow consumers to distinguish between edible and non-edible parts of the food package.

DRIVING FORCES FOR DEVELOPMENTS IN ACTIVE PACKAGING TECHNOLOGY

The two major factors responsible for the developments in active packaging is having extended shelf life and accessible food products at sensible rates. These qualities contribute to heightened requirements for longer shelf life for processed foods and packaged fresh foods. Continued growth for organic foods, in-store prepared foods and other foods containing fewer or no preservatives will boost opportunities for oxygen scavengers in sachet, label or film forms for food security. Additionally, gains will be supported by new mandates aimed at improving food safety and by the leveraging of smartphone applications to bring interactivity to packaging (Freedonia, 2011). There has been an increased demand for innovative ways of packaging systems because of rise of disposable incomes per household, popularization of nuclear family and population increase. Consumers having taste buds to try different food products, becoming health conscious due to which focus has been towards health drinks and foods, have also been considered one of the driving forces for active packaging. Retailers-convenient storage and distribution network, modern retail network, availability, display, doorstep delivery add on to the increasing need for an innovative food packaging technique which could be sufficed by active packaging. When one considers manufacturers point of view, developing a new value adding product along with the use of innovative packaging system shall provide a boost in the field of active packaging. Besides the migration concerns, the concept of active packaging systems has been gaining a lot of popularity as it provides high quality of food, food safety and thus ensuring food security.

MARKET TRENDS OF ACTIVE PACKAGING

World Market: The global market for active and intelligent packaging technology is expected to grow from USD 13.75 billion in 2016 to USD 23.38 billion by the end of 2021 at a CAGR of 9.25% (<https://www.mordorintelligence.com/industry-reports/active-and-intelligent-packaging-market-industry>). Further, the CAGR is expected to increase over the next decade to 11.7% approximately USD57 billion by 2025. It has been predicted that the demand for active and intelligent packaging shall expand at the rate of 7.3% annually and its market is expected to reach USD4.0 billion by the year 2019. In this, the active packaging sector will experience the growth rate of 5.2% targeting to USD2.5 billion by the year 2019 (Freedonia group, 2015). It has been observed that the major market for active and intelligent packaging is North America, holding the largest share of 35.1%. This is followed by the Europe market as the focus of the Europe market has changed towards sustainable market and stringent regulation (Anon, 2011). The prime segment of active packaging is oxygen scavenger and moisture absorber, growing at CAGR of 8% and 11.9% respectively (Anon, 2011b).

Fruits and vegetables

Fruits and vegetables, either fresh or minimally processed, are vulnerable to microbial attack and undergo unfavourable biochemical changes during storage. Respiration is a metabolic process, occurring in all living cells, which involves breakdown of organic matter into simpler products. O₂ from the surrounding atmosphere is taken by the fruits and vegetables for oxidative reduction of respiratory substrates (viz. carbohydrates, organic acids etc.) to carbon dioxide, water and heat (Nayik and Muzzaffar 2014). This energy (in the form of heat) causes an increase in the surrounding temperature of the produce. Respiration contributes to natural ageing process and subsequent deterioration in the living tissues. Thus, greater the respiration rate, the higher the loss of nutritional value of food, loss of sealable weight, poorer flavor and thus, deterioration in the quality of food. This is so because substrates present in these living tissues cannot be replenished once the fruit or vegetable has been removed from the plant. (Nayik and Muzzaffar 2014). In other words, the continuous respiration of fresh produce results in the increase of carbon dioxide content in the package. Simultaneously, humidity is also produced in the

headspace leading spoilage of fruits and vegetable tissue. It has been observed that ethylene production accelerates the ripening and senescence, hence, addition of ethylene scrubbers with packaging materials seems to be an attractive alternative. Chemical ethylene scrubbers are the most commonly used instruments to control the ethylene concentration during postharvest storage (Brackmann et al., 2015). Various active packaging systems can be employed to minimize the spoilage of fruits and vegetables such as oxygen scavengers, CO₂ emitters, desiccants, antimicrobial compounds.

Meat, meat products and fish products

Flesh foods including meat, poultry and fish are susceptible to rapid microbial spoilage. Packaging fresh meat is carried out to avoid contamination, delay spoilage, permit some enzymatic activity to improve tenderness, reduce weight loss, and where applicable, to ensure an oxymyoglobin or cherry-red colour in red meats at retail or customer level (Brody, 1997). Meat spoilage is often accompanied by slime and tissue softening. These fresh muscle foods undergo rapid adverse changes in their organoleptic and sensorial qualities and are thus, rejected by the consumers hence causing economic losses. Colour is one of the crucial aspects which influence the consumer's purchasing decision. The meat protein, myoglobin, usually exists in one of three chemical forms. The purple coloured pigment present, deoxymyoglobin oxygenated to cherry red oxymyoglobin. Further, oxymyoglobin is oxidized to metmyoglobin. This metmyoglobin results in discoloration associated with lack of freshness. Therefore, to minimize the deleterious effects of oxygen, oxygen scavengers have been used for packaging of meat and meat products.

The scientific literature contains a number of references to studies, which examine the influence of oxygen scavenger sachets on fresh beef discoloration (Day, 2008; Kerry et al., 2006). Martinez et al. (2006) reported that fresh pork sausages stored in 20 % CO₂: 80% N₂ plus an oxygen scavenger (Ageless® FX-40) for up to 20 days at 2 ± 1 °C had reduced psychrotrophic aerobe counts and an extended shelf-life in terms of colour and lipid stability. Comprehensive reviews on antimicrobial food packaging have been published by Appendini and Hotchkiss (2002) and Suppakul et al. (2003). An additional study regarding the combination of high pressure processing (800 MPa) and antioxidant active packaging (rosemary extract) on minced chicken breast and thigh patties showed that active packaging is capable of delaying the lipid oxidation generated by the application of high pressure and thus extend the shelf life of the product (Bolumar et al. 2011).

Fish and fishery products have gained considerable attention as a good source of high quality proteins, essential vitamins and minerals and polyunsaturated fatty acids (Mohan et al., 2010). The biochemical and enzymatic reactions are responsible for the spoilages of fish characteristics thereby, making it unsuitable for human consumption. The degradation of lipids and proteins accompanied by release of biogenic and volatile amines is responsible for bad odour and spoilage in fish products. Sivertsvik (1997) evaluated the effect of an iron-based O₂ scavenger on different seafood products and reported an extension of shelf life for oxygen-sensitive products. Goncalves et al. (2004) studied the effects of O₂ absorber on the gilthead seabream (*Spratus aurata*) and reported the extension of shelf-life considerably compared to air packed samples. The effects of iron based O₂ absorber on the quality and safety of fresh water cat fish (*Pangasius sutchi*) and seer fish (*Scomberomorus commerson*) during chilled storage were studied (Mohan et al., 2008, 2009a, b). The commercial O₂ absorbers used were effective in reducing the O₂ content in the packs up to 99% within 24h. This decreased O₂ content reduced the oxidative changes, volatile amine formation and total mesophilic bacterial counts significantly compared to air packed samples (Mohan et al., 2008, 2009a, b). The use of O₂ absorber extended the shelf life of catfish to 20 days compared to only 10 days for air packed samples (Mohan et al., 2008). In the case of seer fish, O₂ scavenger packed samples were found acceptable up to 20

days compared to 12 days for control air packed samples (Mohan et al., 2009a). Relatively faster degradation of ATP and presence of its degradation products was reported for seer fish packed in control air packs compared to samples packed with O₂ absorber (Mohan et al., 2009a). Apart from the shelf life extension, use of O₂ scavenger altered the spoilage microflora of seer fish from gram negative particularly *Pseudomonas* and H₂S producers to gram positive mainly *Brochothrix thermosphacta* and *Lactobacillus* spp. (Mohan, 2008). Nanopack Technology and Packaging SL in collaboration with IRTA is developing a range of interleavers (Sanic films) able to extend the shelf life of vacuum packed meat products (Nanopack, 2014).

Milk and milk products

Fresh milk gets spoiled due to growth of microorganisms and the flavor of milk becomes unacceptable when bacterial count reaches to 107 CFU/ml. Pasteurized milk has very short shelf life in tropical countries even at refrigerated temperatures. Pasteurized milk could benefit from antimicrobial packaging treatments (Rooney, 1993). Milk and milk products have gained wider acceptance, however oxidative reactions are a major deteriorating factor. Dairy products especially cheeses owing to their higher water activity are susceptible to microbial growth. The quality of milk pomade sweet – sherbet packed in different packaging materials (Multibarrier 60, met.BOPET/PE, Aluthen), incorporated with iron based oxygen scavengers was evaluated for its physiochemical properties before and after packing and storage (Ungure et al., 2012). From their experiments, it was concluded that met.BOPET/PE and Aluthen film packaging if incorporated with oxygen scavenger could prove to be a promising packaging material for sherbet packaging and long term storage. In another study, multilayer co-extruded films made of high density polyethylene (added with titanium dioxide), ethylene vinyl alcohol and a layer of low density polyethylene containing the antioxidants butylated hydroxyanisole (1.5%), butylated hydroxytoluene (1.5%) and α-tocopherol (4%) were employed in packaging of whole milk powder (Restrepo et al., 2009). The results from this study suggested that multilayer co-extruded films provide an adequate light-barrier for whole milk powder and the film added with α-tocopherol contributed to the protection of vitamin A degradation. Similar results have also been reported by Soto et al., 2011 on the evaluation of sensorial properties of whole milk powder upon usage of antioxidant active packaging. One form of active packaging utilizes the incorporation of enzymes to facilitate in process processing. These employ bioactive compounds such as enzymes and peptides that immobilize the moiety via entrapment or physical adsorption. Appendini and Hotchkiss (1997) investigated the efficiency of lysozyme immobilized on different polymers and determined that the combination of cellulose triacetate containing lysozyme produced great antimicrobial activities. Goddard et al. (2007) demonstrate that this concept operates in removing lactose from milk. Lactase could be incorporated to the wall of the package container. A British patent assigned to Tetra Pak International AB describes incorporation of lactase to pasteurized or sterilized milk prior to packaging in order to split lactose after packaging.

Dried foods CO₂ absorbers in coffee powder

Dried foods such as milk powder, dried soups, nuts, dried fruits and ground coffee are very much sensitive to moisture and oxygen. Such dried foods are of higher significance both nutritionally and convenience point of view. To check the browning in dried fruits, SO₂ lost through absorbers may solve this problem. Kraft foods employed iron oxide sachets within the steel cans of roasted and ground coffee to absorb excess CO₂ emitted by coffee. Hence, CO₂ absorbers are used to minimize flavor volatilization. These sachets contain Ca(OH)₂, in addition to iron powders absorb CO₂ as well as O₂. Charles et al 2016, studied the absorption kinetics of two commercial O₂ and CO₂.

Active ingredients used in active packaging

The active ingredient used is generally a brown/black powder or aggregate; non-toxic in nature. Another scavenging medium could be the use of a transparent packaging plastic. Antimicrobial active packaging system has become a promising system for maintaining product quality and safety for a longer period of time. Japan introduced the wasabi and ethanol as the active ingredients to be incorporated in the active packaging systems. For this, different organic acids such as citric acid, lactic acid and ascorbic acid are usually applied as dip. The following food -grade antimicrobial agents can be used for antimicrobial food packaging systems; organic acids and their salts (acetic acid, benzoic acid, potassium sorbate, sodium benzoate, sorbic anhydride, benzoic anhydride, alkyl (ethyl, methyl, propyl) paraben, fatty acids (lauric acid, palmitoleic acid, glycerol mono-laurate), chelating agent (EDTA), metals (silver, copper, zirconium, titanium oxide), enzymes (lysozyme, peroxidase, glucose oxidase), polypeptide (lactoferrin), bacteriocin (nisin, pediocin, lacticins), chitosan, antioxidants, antibiotics, fungicides, sanitizing gas, sanitizers, phenolics, plant volatiles, plant spice/spice extracts, plant essential oils (cinnamon, oregano, lemongrass), nitrites and sulphites, and probiotics (Lee, 2010).

Migration in active packaging systems

The three major components of active food packaging systems are the packaging material, food and headspace. The two types of food systems are: package and food system and second is food/ packaging/headspace system (Han, 2003). The former involves diffusion of active substances between the packaging material and the food constituents and partitioning at the interface is the main migration mechanism in this type of food system. The latter system involves evaporation or equilibrated distribution of the active substance between the headspace, the packaging material, and the food (Singh, 2003). Figure 1 depicts the active packaging mechanism. The control release rates and migration amount of active substances are very crucial parameters in active packaging systems. Controlled migration of the active compound from the packaging material into the food enable not only the initial inhibition of undesirable microorganisms but also create a residual activity over time, during transportation, storage and distribution of food (Cutter, 2002). Controlled release packaging is well-suited for controlling continuous food degradation reactions, such as microbial growth and lipid oxidation, because constant replenishment of active compounds can maintain safety and quality. Controlled release may be defined as a process by which one or more active ingredients are made available at a desired site and time at a specific rate. Controlled release offers the following advantages: (a) active ingredients are released at controlled rates over prolonged periods of time, (b) ingredient loss during processing and cooking can be avoided or limited due to increased stability, and (c) reactive or incompatible components can be separated (Pothakamury and Barbosa-Cánovas 1995).

Controlled Release Systems in Packaging

The majority of release profiles by a controlled release system can be categorized into zero-order release and first-order release (Baker, 1987). Zero-order release is the simplest profile where the release rate remains constant until the package no longer contains an active compound. During first-order release kinetics, the release rate is proportional to the mass of active compound contained within the package. The rate declines exponentially with time in first-order release, approaching a release rate of zero as the package approaches emptiness. Researchers at Virginia Tech have studied poly(lactide-co-glycolide) films loaded with BHT, BHA, and α -tocopherol and their subsequent release into dry milk products (van Aardt et al., 2003).

Moisture Absorbers

The presence of moisture in foods such as fruit and vegetables, fish, meats, poultry, snacks, cereals, dried foods, etc. is a common cause of food spoilage. The loss of water takes place due to respiration in foods that result in quality losses and reduction in their shelf-life. An effective way of controlling excess water accumulation in a food package that has a high barrier to water vapour is to use a moisture absorber (Ozdemir and Floros, 2004). The moisture absorbers bind water, either in the form of vapour or liquid, thereby preventing the food product from retaining water and getting spoiled. These are usually prepared in the form of sachets, pads or sheets. The most common moisture absorber is silica gel because it remains dry and free flowing even when saturated (Day and Potter, 2011). For packaged dried food applications, desiccants such as silica gel, calcium oxide and activated clays and minerals are typically used tear-resistant permeable plastic sachets (Dobrucka and Cierpiszewski, 2014). In addition to moisture-absorber sachets for humidity control in packaged dried foods, several companies manufacture moisture-drip absorbent pads, sheets and blankets for absorbing liquid water in foods having higher moisture content such as fruits, vegetables, meats, fish and poultry (Day, 2008). For dual-action purposes, these sachets may also contain activated carbon for odour adsorption or iron powder for oxygen scavenging (Rooney, 1995). Molecular sieves such as zeolites have high affinity for water and they can absorb upto 24% of their weight in water (Brody et al., 2011). In addition to moisture absorbers, humidity control sachets are also sold in markets. Desiccants are being incorporated into polymers in order to protect food products and pharmaceuticals against moisture uptake. One such approach being used by Fraunhofer IVV which involves using calcium oxide in materials. MiniPax® Sorbent silica gel packets are constructed with extremely durable, tear resistant, medical grade Tyvek® spunbonded polyolefin (<http://www.nutrimedgroup.com/pdf/MiniPax2.pdf>). Humidipak (Humidipak Inc.) is commercially sold as a humidity control sachet that uses a saturated solution of substances to maintain the optimum humidity in the package. It works by absorbing and releasing moisture in response to the surrounding environment (Day and Potter, 2011). Some other moisture absorbers that have known to extend the shelf life of food products and have been used commercially as sheets, blankets or trays include Toppan sheet™ (Toppan Printing Co. Ltd Japan), Thermarite™ (Thermarite Pty Ltd, Australia), Luquasorb™ (BASF, Germany) etc. (Day, 2008).

Mechanism of action: In their own moisture-permeable sachets, desiccants absorb water vapour from the contained product and from the package headspace, and absorb any water vapour that enters by permeation or transmission through the package structure. As separate entities within packages, active packaging sachets, pouches, patches, coupons, labels, etc., are not often integral to the package—a semantic differentiation. Desiccant pouches are widely used in the packaging of hardware and metal goods.

OXYGEN SCAVENGERS

The best-known and most widely used active packaging technologies for foods today are those engineered to remove oxygen from the interior package environment. Oxygen scavengers reduce oxidative effects in the contained products such as breads, cakes, cooked rice, biscuits, pizza, pasta, cheese, cured meats and fish, coffee, snack foods, dried foods and beverages. Most oxygen scavengers in commercial use today are gas-permeable, flexible sachets containing reduced iron (i.e., iron not in the fully oxidized state) particles inserted into food and other packages from which air is initially removed by vacuum or by flushing with inert gas. During the last two decades of the twentieth century, commercial incorporation of oxygen-removal materials directly into a package structure occurred with varying results. Several applications for beer and juice bottles became

commercial in 2000. The goal of active packaging, in conjunction with other food processing and packaging, is to enhance preservation of contained food and beverage products. For example, to optimize the effects of oxygen scavenging, oxygen should first be removed from the product during processing and packaging operations. The oxygen must also be thoroughly removed from the package interior and the package materials, and the package structure, including materials and closure, must be barriers to further oxygen entry. In other words, oxygen scavenging complements good oxygen-control practices. In addition, oxygen is certainly not the only vector that can influence the quality of the contained food. For example, moisture gain or loss, light, nonoxidative reactions, microbiological growth, and enzymatic activity may all, individually or collectively, be involved in food-product deterioration. Worldwide development efforts devoted to oxygen removal have indicated that analogous efforts by the same and parallel research teams continue to be applied to oxygen scavenging and are being studied for other active packaging forms. Oxygen is one of the major causes for food spoilage and proliferation of moulds, proliferation of aerobic bacteria and insects. Oxygen scavengers are substances added in the packaging system to remove oxygen from the food package. They are based on the oxidation of iron powder or using enzymes to scavenge oxygen. They prevent oxidative damage to oils and fats to prevent their rancidity and prevent discoloration in plants and muscles pigments. They are able to reduce the oxygen concentration to less than 0.01% (Rooney, 1995; Vermeiren et al., 1999). Different studies show that the use of scavengers led to faster reduction and to lower levels of residual oxygen, as compared to nitrogen flushing (de Fátima, 2001) The most common substances used are iron powder and ascorbic acid (de Fátima, 2001). The substance is usually contained in sachets made of a material highly permeable to air, bottle closures, plastic film matrix etc. Initial researches suggest that these sachets employed inside the food packages have been shown to effectively remove oxygen from the packages of bananas, avocados, persimmons etc. For shelf life extension of kleo cheese, an investigation was done by Muizniece-Brasava et al. (2011), utilizing active packaging in combination with modified atmosphere packaging (MAP). An iron-based oxygen scavenger sachet of 50 cc obtained from Packaging Solutions OÜ and modified atmosphere consisting of carbon dioxide CO₂ (E 290) 30% and nitrogen N₂ (E 941) 70% were utilized. By use of both, usual MAP conditions as well as with oxygen scavenger commitment in the pouch, the shelf life was extended, good outside appearance and lactic acid aroma was observed (Muizniece-Brasava et al., 2011). The oxygen scavengers prevent oxidation phenomena: rancidification of fats and oils and consequent emergence of off-odors and off-flavors, loss or change of colors characteristic of food, loss of oxygen-sensitive nutrients (vitamins A, C, E, unsaturated fatty acids, etc.) (Lee et al., 2010). A recent study showed the combined effect of an O₂ absorber and citrus extract (0.1 and 0.2 ml/100 g), on shelf life extension of fresh ground chicken stored at 4°C. The citrus was found to have a preservative effect on the shelf life of chicken which increased upto 4-5 days as compared to the control samples (Mexis et al., 2012).

Oxygen scavengers must satisfy certain requirements (Rooney 1995):

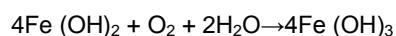
- a. Harmless to human body
- b. Absorb oxygen at an appropriate rate
- c. Not to produce toxic substances, unfavourables gases or odours.
- d. Constant quality and performance
- e. Compact in size
- f. To absorb maximum oxygen
- g. Economically priced.

Ageless® is one of the most widely used oxygen scavenger supplied by Mitsubishi. It may be supplied in different formats: sachet, to be placed in the primary package, pressure-sensitive label to be affixed in the internal surface of the package or

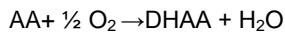
card for product support (de Fátima, 2001). Some other important O₂ absorbent scavengers that have been used previously or are being currently utilized are ATCO® O₂ scavenger (Standa Industrie, France), Freshilizer® Series (Toppan Printing Co., Japan), FreshPax® (Multisorb Technologies Inc. USA), ZerO2® (CSIRO), OS2000® (Cryovac: Sealed Air Corporation, USA) and OSP® (Chevron). Another scavenging technology is based on catechol oxidation as suggested by Ahvenainen (2003). Since catechol is an organic compound, it passes metal detectors. Tamotsu is based on this technology and is used for dried products like spices, tea, freeze dried foods (Vermeiren, 2003). The different mechanisms of action of oxygen scavengers are hereby summarized:

Mechanism of action

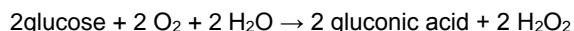
- a. Iron based: This system is based on the oxidation of iron and ferrous salts (provided in the packet) that react with water provided by food to produce a reaction that moisturizes the iron metal in the product packaging and irreversibly converts it to a stable oxide. The iron powder is contained within small oxygen permeable bags that prevent contact with food. Oxygen scavenger systems that are based on iron oxidation reactions are explained by the following equation (Prasad et al 2014):



- b. Ascorbic acid based: (Cruz 2012). The ascorbic acid is another oxygen scavenger component which is based on ascorbate oxidation to dehydroascorbic acid. The ascorbic acid reduces the Cu²⁺ to Cu⁺ to form the dehydroascorbic acid. Further, the cuprous ion forms a complex with O₂ resulting in cupric ion Cu²⁺, superoxide anionic radical. In the presence of copper, the superoxide anionic radical leads to the formation of O₂ and H₂O₂. After that the copper ascorbate complex converts H₂O₂ to H₂O without the formation of OH, which is a highly reactive oxidant. The reaction below depicts the processing of active system of oxygen absorber by ascorbic acid. It can be summarized as:

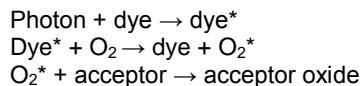


- c. Enzyme based: It is usually based on the oxidation carried out by enzyme glucose oxidase (Vermeiren et al 2000). The glucose oxidase transfers two hydrogens from the -CHOH group of glucose, that can be originally present or added to the product, to O₂ with the formation of glucono-delta-lactone and H₂O₂. The lactone then spontaneously reacts with water to form gluconic acid (Labuza and Breene, 1989). In such reactions a natural contaminant is found by default in the preparation of glucose oxidase, thus catalase reacts with H₂O₂ forming H₂O and O₂ effecting the systems efficiency. Hydrogen peroxide formed is broken down to peroxide due to its undesirable characteristic.



where glucose is the substrate.

- d. Photosensitive dye oxidation: Another technique of oxygen absorption is a photosensitive dye impregnated onto a polymeric film. When the film is irradiated by ultraviolet (UV) light, the dye activates the O₂ to its singlet state, making the oxygen-removing reaction much faster (Cruz 2012)



Classification of oxygen scavengers

The oxygen scavengers can be classified according different characteristics or properties related to their activity or their form (Schroeder, 2001). These can be classified on the basis of activation mechanism.

- **Auto activated systems :** There are some scavenging compounds that start absorbing oxygen immediately when exposed to oxygen or air at normal ambient humidity and temperature. Many unsaturated polymeric scavengers, or natural biological scavengers as enzymes, vitamins and fatty acids do not require any triggering step to initiate the reaction, and they are normally characterized by fast reaction and high scavenging capacity. Nevertheless, the auto activated systems need particular care during the handling, the process and the storage, to avoid a considerable reduction of their scavenger effectiveness.
- **Water activated systems:** The water is an essential component of many oxygen scavenging reactions mechanisms. It can act as solvent or as swelling agent. In particular, when the chemical reagents are in the crystalline form or they are coated with a low-permeability material, the water have to dissolve the reagents in order to promote the oxidation. Differences in scavengers arise, however, with the source of the water itself. Many scavengers require the addition of water as vapour to begin the oxygen absorption. These scavengers are often designed to be incorporated into retortable plastics packaging that will undergo steam retorting at about 120°C. In these cases, water vapour permeation from the outside is sufficient to let the process to start. For other systems it is necessary to fill the package with a liquid substance to activate the scavenger. In this case the potential source of water is the product itself; therefore, these OS systems are mainly used for beverage applications, as juice, beer, tea etc.
- **UV activated systems:** Many oxidation reactions need continuous or brief exposure to light, or ultra violet radiation for starting. The UV activated systems are based on photosensitized OS reactions and their technology consists in photosensitive dye impregnated or coated on a polymeric film. In UV activated systems, irradiation is done by UV light resulting in the activation of O₂ in its singlet state. However, the limiting factor in this system is the UV radiation. This processing have to be done after completion of food packing, taking sensitivity factor of the food products into account as such radiation may compromise the properties of the food product. -Although the photo activators are low molecules that can easily migrate through the sachet or the lid or the polymer structure. These materials are then not suitable for the food contact.
- **Other mechanisms:** There are many researches are going on in the field of exploring new active packaging systems for example, Toppan Printing Co., Japan, for example, has patented a system that use magnetic fields to activate scavenging compounds (Fukuyoshi, 2001).

In order to design a performing package, it is important to consider the reaction speed of the scavenger system and to compare this characteristic to the oxygen sensitivity of the food product. The reaction speed can be dependant by the chemical nature of the scavenger, by the storage conditions or by the OS system itself. In particular when the scavenger

compounds are inserted into polymeric matrix the reaction can be delayed since the oxygen, or other reagents of the reactions (i.e. the water) have to reach the active site inside the polymer matrix, before reacting.

CO₂ ABSORBERS/EMITTERS

CO₂ absorbers/emitters are generally used in coffee, fresh meat and fish, nuts and other snack food products and sponge cakes. The presence of carbon dioxide in the packaging system suppresses the microbial growth in it. The permeability of CO₂ is about 3 to 5 times higher than that of O₂ in most plastic films, thus, it is should be essentially present within the package to maintain the desired concentration. de Fatima (2001), had also suggested that carbon dioxide generators may be used in packaging for fresh produce where an increased concentration of CO₂, combined with decreased O₂ concentration, reduces the respiration rate thus increasing the product's shelf-life. Another application suggested by de Fatima (2001) for carbon dioxide emitters was the packaging of meat products where a high level of CO₂ might inhibit microbial growth. Furthermore, freshly roasted or ground coffees emit substantial amounts of carbon dioxide. They are to be packed very closely since they can absorb moisture as well as oxygen which may lead to loss of its aroma and flavourful constituents. However, Day (2008) stated that if coffee is hermetically sealed in packs directly after roasting, the carbon dioxide released will build up within the packs and eventually cause them to burst. To avoid this problem, he suggested two solutions that are currently being used. The first is to use packaging with patented one-way valves that will allow excess carbon dioxide to escape. The second solution is to use dual action of oxygen and carbon dioxide and carbon dioxide scavenger system. This second solution is more commonly and commercially viable system for canned and foil pouched coffees especially in Japan and the USA (Day, 2003; Rooney, 1995). Also, carbon dioxide is added into the food packages to increase internal environmental gas to suppress microbiological growth and extend the shelf-life of food products. CO₂ absorbers (sachets) usually consist of either calcium hydroxide and sodium hydroxide or potassium hydroxide, calcium oxide and silica gel. Other sachets are available based on either ascorbic acid and ferrous carbonate or ascorbic acid and sodium bicarbonate that absorb oxygen and generate an equivalent volume of CO₂ thus avoiding package collapse or development of partial vacuum (Robertson, 2012). A study investigated the effect of MAP on strawberries in presence of two different carbon dioxide scavengers and one oxygen scavenger throughout storage at 4° C for four weeks and it was found that this preserved the strawberries very efficiently (Aday et al., 2011).

CO₂ generators that have been employed commercially are: Ageless (Mitsubishi Gas Chemical Co., Japan), Freshilizer (Toppan Printing Co., Japan), FreshPax (Multisorb Technologies Inc., India), Verifrais™ package, SARL Codimer (Paris, France). Other activated carbon-based scavengers are SendoMate from Mitsubishi, which is based on a palladium catalyst, Hatofresh System from Honshu Paper, which is based on activated carbon impregnated with bromine-type inorganic chemicals and Neupalon from Sekisui Jushi (Japan) (Zagory, 1995).

Mechanism of action: Microbial activity is suppressed by the application of carbon dioxide. Relatively high CO₂ levels (60 to 80%) inhibit microbial growth on surfaces and, in turn, prolong shelf life of packed food. Therefore, a harmonizing approach to O₂ scavenging is the impregnation of a packaging structure with a CO₂ generating system or the addition of the latter in the form of a sachet (Ha et al 2001). The permeability of CO₂ is higher than O₂ in case of plastic films, therefore it is desirable to be produced within the package (Suppakul et al, 2015). One of the advantages of high level of carbon dioxide has the potential

to affect the changes in the certain food products such as fresh meat, poultry, fish and cheese packaging though oxygen-free environment alone is insufficient to retard the growth of *Staphylococcus aureus*, *Vibrio* species, *Escherichia coli*, *Bacillus cereus* and *Enterococcus faecalis* at ambient temperatures. O₂ and CO₂ absorber inhibited the growth of *Clostridium sporogenes* (Scannell et al. 2000).

ETHYLENE SCAVENGERS

Ethylene is produced during ripening of fruits, vegetables and other horticultural products that have both positive as well as negative effects on them. The positive effects include catalyzing the ripening of fresh produce while the negative effects are responsible for a wide variety of undesirable changes in them. It has long been recognized as a problem in post-harvest handling of horticultural products. Fruits and vegetables produce ethylene, aldehydes and other gases during ripening which further promote the ripening process. This leads to their softening and decay under the action of microorganisms. The removal of this gas from storage chambers and packages of fruits and vegetables is, therefore, very crucial. Ethylene is a highly reactive gas and can be altered in many ways, such as chemical cleavage and modification, absorption, adsorption, etc. Ethylene scavengers are an important active packaging system in the commercial world of fresh fruits as it is highly required to remove ethylene. A study by Kudachiker et al (2011) investigated bananas kept under active and passive MAP 12±1 °C and 85-90% RH. The experiment employed green keeper (GK) ethylene scavenger. It was concluded that the shelf life of bananas under MAP + GK was enhanced upto 5 and 7 weeks as compared to openly kept control bananas. In order to remove ethylene from the package containing broccoli and prevent its yellowing and quality loss to extend its shelf life, a novel ethylene scavenger supported by acidified activated carbon powder (AACP) was developed (Cao et al., 2015). Another recent investigation by Ali et al. (2015), on the influence of different packaging materials and ethylene absorbent on biochemical composition, antioxidant and enzyme activity of apricot, made it quite evident that apricot harvested at commercial maturity stage and packed with low density polyethylene films along with ethylene scavenger (KMnO₄) can be successfully stored at ambient conditions up to two weeks.

Although many ethylene adsorbing substances have been elucidated in the patent literature, the major ones as reviewed by Zagory (1995) are: potassium permanganate, bentonite, Kieselguhr, and crystalline aluminosilicates, e.g., zeolites, Fuller's dust, Brick dust, silica gel and aluminium oxide and have been known to adsorb ethylene. The most commonly used absorbers are based on potassium permanganate, activated carbon and activated earth. Another example of absorber is Charcoal loaded with palladium chloride can oxidize ethylene to acetaldehyde, decelerating the maturation rate of climacteric fruits (Lorens et al., 2011). Some commercially used ethylene scavenger sachets are Evert-Fresh (Evert-Fresh Co, USA), Peakfresh (Peak Fresh Products, Australia), Ethylene Control (Ethylene Control Incorporated, USA) (Ozdemir and Floros, 2004). LDPE and HDPE polyethylene films used as packaging material. These films absorb ethylene; ethanol, ethyl acetate, ammonia, and hydrogen sulfide. These films keep food fresh for longer and eliminate odors (Prasad et al 2014).

Mechanism of action: Mechanism of ethylene scavengers works by using potassium permanganate, which oxidizes ethylene to carbon dioxide and water. Potassium permanganate works by oxidizing ethylene resulting in change of color from purple to brown. This color change is the indicating factor for reduction in ethylene absorbing ability, but due its toxic nature, potassium permanganate cannot be used in direct contact with food. Permanganate content used is generally between 4% to 6% (Abe and Watada 1991). Other systems are based on their ability to absorb ethylene, either alone or with the help of any oxidizing

agent. Smith et al (2009), studied the characteristics of palladium, having higher ethylene adsorption capacity than permanganate-based scavengers under conditions of high relative humidity.

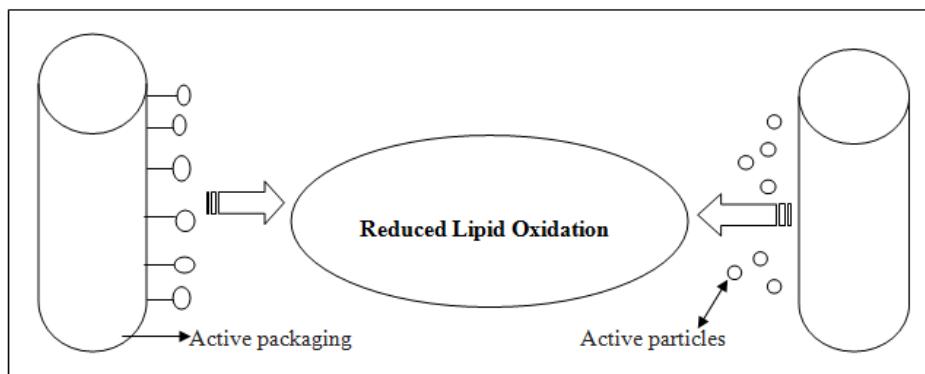
ANTIOXIDANTS

Antioxidants interrupt the formation of free radicals which are formed as the intermediate products of lipid oxidation in food products like nuts, meats, fish etc. Oxidation of fat is a major cause of food deterioration, reduction in nutritional quality and loss of texture and functionality in muscle foods. It can be prevented by adding antioxidants in the packaging material. Such packaging is intended to prevent or slow down the oxidation reactions that affect the quality of food (Pereira et al., 2010). In 1986, Rho et al. showed that coating the interior surface of a polyethylene film package with t-butylhydroquinone (TBHQ) extended the shelf life of contained deep-fried noodles. Dr. Joseph Miltz and his co-workers (1988) demonstrated that when butylated hydroxy toluene (BHT) was incorporated into high density polyethylene film, the shelf life of contained oat cereal was increased. Thus, the researchers of the time concluded that incorporating antioxidants into the plastic film of the package was effective in increasing the shelf-life of the food products. Two modes of action for antioxidant packages were elucidated by Gómez-Estaca et al. in 2014. First was the release of antioxidants into the food and second, the scavenging of undesirable substances such as oxygen, radical oxidative species or metal ions from the food or headspace of the package. Antioxidant packaging materials are being developed by incorporating the active compounds in the polymer matrix or on the polymeric film surface. From a technological point of view, the agent (or the reactive substances which produce the agent) is intimately mixed with the polymer, either by coating technology or polymer melting technology (Gómez-Estaca et al. 2014). Problem arises when antioxidant content decreases due to diffusion through the film and it subsequent evaporation during storage. Thus, an extra layer of film can be added which decreases the diffusion of the antioxidant. Antioxidants can be incorporated in the active packaging system of oil, nuts, butter, fresh meat, meat derivatives, bakery products, fruits and vegetables.

In last years, different antioxidants such as lemongrass essential oil (Ahmad et al., 2012), α -tocopherol (Graciano Verdugo et al., 2010), green tea extract, cinnamon oil or clove oil (Phoopuritham et al., 2012), were incorporated into the food packaging to extend the shelf-life of sea bass slices, corn oil and vegetable oil respectively (Sanches-Silva et al., 2012). Migration of α -tocopherol from a multilayer active packaging (made of high-density polyethylene, ethylene vinyl alcohol, and a layer of low-density polyethylene containing the antioxidant α -tocopherol) showed a delay in lipid oxidation in whole milk powder (Nerin et al., 2006). A recent study conducted by Wrona et al. (2015) proved that active packaging is a promising approach to extend the shelf-life of packed fresh mushrooms without compromising their fresh status. Four different active agents were incorporated into the packaging material to extend their shelf-life: sodium metabisulphite combined with citric acid; green tea extract; cinnamon essential oil and purple carrot extract. The sulphur dioxide-based packaging maintained the mushrooms white and appealing to consumers for a longer time than conventional packaging. Green tea extract at high concentrations maintained white colour of mushrooms as compared to blank as well as other samples (Wrona et al. 2015). In another study by Contini et al. (2011), two active packagings consisting of PET trays sprayed with citrus fruit extract was developed and it was found that lipid oxidation of meat samples in citrus fruit extract coated trays was significantly lower than the uncoated trays; hence, it was concluded that active packaging based on natural antioxidant compounds, obtained from citrus fruit extract, showed considerable capability in reducing oxidation in cooked turkey meat samples. The use of active packaging system showed a preservative effect on foal meat stored under refrigeration from spoilage and lipid oxidation. This was demonstrated in a study conducted by Lorenzo et al. (2014) where in two films were prepared, one containing 2% oregano

essential oil and other with 1 % green tea extract and foal meat was packed in them. It was found that the shelf life, quality of the foal meat and its sensorial properties were enhanced.

Figure 1: A schematic representation of use of antioxidants in active packaging



Mechanism of action: Antioxidants and oxygen interceptors incorporated into package materials, such as tocopherols (vitamin E), have emerged in recent years and are increasingly employed to combat odours generated in plastic processing. Tocopherols, which are non-volatile, have not replaced volatile butylated hydroxyanisole/ butylated hydroxytoluene (BHA/BHT) which migrate into foods in product antioxidant applications, but they appear to be new antioxidants of choice for mitigating the effects of oxygen (Fig. 1). Entities such as oxygen scavengers/interceptors react with oxygen to form new compounds. Oxygen absorbers may remove oxygen by any means, including physical. Antioxidants react with free radicals and peroxides to retard or block the actual oxidation reactions. Sequestering agents tie up inorganic catalysts that might otherwise accelerate adverse oxidative reactions. Members of the food technology and packaging communities have long regarded package materials as an ideal reservoir and delivery vehicle for antimicrobial compounds. For many years, sorbic acid has been incorporated sparingly on the interior of package structures as an antimycotic in a limited number of dry food packages. The obvious benefits of sorbic acid as a mold and yeast inhibitor have been one foundation by which numerous other antimicrobial agents have found their way into food package materials. Unfortunately, most antimicrobial agents also exhibit toxicity when they enter the food from the package and would be consumed as part of the food. Thus, actual commercialization has been proceeding slowly, except in Japan where several compounds have been reported to function effectively as antimicrobials in commercial packages. As with oxygen scavengers, the major technological and commercial successes for antimicrobials have been achieved by Japanese organizations for packaging Japanese products in Japan.

An active film from chitosan incorporated with aqueous green tea extract (GTE) as a natural antioxidant was developed in an experiment conducted by Siripatrawan and Harte (2010) and the results suggested that addition of GTE improved mechanical, water vapour barrier and antioxidant properties of the resulting films, thus improving the shelf life of food products. However, more studies are required before using this film as an active packaging of food products.

ANTIMICROBIAL PACKAGING

Antimicrobial packaging applications are concerned with microbial safety as well as prevention of growth of spoilage microorganisms in order to increase the shelf life of food products. Antimicrobial packaging systems consist of packaging materials, in-package atmospheres and packaged foods and thus, are able to kill or inhibit microorganisms that cause food borne illnesses (Han, 2003). Direct addition of antimicrobials could result in some loss of their activities because they diffuse into the food matrix. The antimicrobial active packaging technology based on antimicrobial agents that are immobilized with the polymeric structure or incorporated in plastic resins, before film casting. The working of antimicrobial packaging can be of two ways: preservatives that are released slowly from the packaged materials to the food surface or preservatives that are firmly fixed and do not migrate into the food products. Both are assumed to control growth of undesirable microorganisms (Cahan et al., 2003). An antimicrobial agent has specific inhibitory activity and mechanism against every microorganism. Dash (2014) suggested five types of antimicrobial packaging viz., volatile antimicrobial substances that are incorporated into a sachet/pad and kept in food package; antimicrobials that are coated or adsorbed onto polymer surface, volatile and non-volatile antimicrobial substances directly incorporated into the polymers, antimicrobials immobilized into polymers by ion or covalent linkages and polymers that are inherently microbial (Appendini and Hotchkiss, 2002). Antimicrobial food packaging is being used for many food products in USA and Japanese markets and can be clubbed with newer technologies like MAP, Radio frequency identification (RFID) or freshness indicators. Chitosan is the natural polymer with inherited antimicrobial property and is one of the ideal biodegradable film (Sung, 2013). A potassium salt of the sorbic acid plays a very significant role as a fungicide called potassium sorbet. It is employed for the preservation purpose to the dairy products, cheese and kinds of dough (Realini & Marcos, 2014).

Table 2: Recent Antimicrobial Nanoparticles Food Application

Antimicrobial Nanoparticles	Food Application	Reference
Silver Nano particles and Titanium oxide (Ag/TiO ₂)	Effect of stable antimicrobial nano-silver packaging on inhibiting mildew and in storage of rice.	Li et al, 2017
Nanocomposite material based on PVC and silver nanoparticles	Inhibition of the proliferation of yeast/molds, <i>B. cereus</i> , and <i>B. subtilis</i> on Bread and thereby extend its shelf life. The use of PVC and Ag nanoparticles on the quality of chicken breast meat.	Cozmuta et al, 2015 Panea et al, 2014
Nano-silver and zinc oxide (ZnO)	Extending the product shelf life and resulting in lower lipid oxidation of chicken breast fillets. Studied the antimicrobial activity of LDPE loaded with nano-silver and zinc oxide (ZnO) for prolonging the shelf life of orange juice	Azlin-Hasim et al, 2016 Emamifar et al, 2010
	Addition of antimicrobial agent to active packaging films for packaging fresh poultry meat, to increase the shelf life.	Akbar and Anal 2014

Chemical antimicrobial agents include fungicides such as imazalil and benomyl, benzoic acid, sorbic acid, silver in polymers, silver-ion containing zeolite, glass systems incorporated into polymers etc. Plant origin antimicrobials include extract of spices such as thyme, oregano etc. Antimicrobial agents produced by microorganisms include bacteriocins such as nisin or pediocin, antibiotics such as natamycin, enzymes such as lysozyme etc. Chitosan is an example of natural antimicrobial polymer

obtained by deacetylation of chitin obtained commercially from shrimp and crabshell. Another natural antimicrobial system that could be used for antimicrobial packaging is the lactoperoxidase system of the milk. The immobilization of lactase and glucose oxidase enzymes on nylon pellets has been investigated with the goal of producing hydrogen peroxide to activate the hydrogen peroxidase systems naturally present in milk (Garcia-Garibay et al., 1995). Also, fungicides are added into waxes and are coated to fruits and vegetables to meet the requirement of antimicrobial food packaging. Such as, LDPE (Low density polyethylene) film was incorporated with Nisin by means of methylcellulose / hydroxypropyl methylcellulose (MC/HPMC) which acted as a transporter (Gemili et al., 2009).

BIOACTIVE COMPOUNDS AS ADDITIVES

These are strong antimicrobial agents against psychrophilic and mesophilic microorganisms present in fresh cut produce (Uyttendaele et al., 2004; Bari et al., 2005). Some natural bioactive compounds like ascorbic acid and N-acetylcysteine have been used to prevent enzymatic browning and conserve the color of freshly cut fruits and vegetables (Rojas Crau, 2009). The most commonly used bioactive compounds that provide health benefits as well as improve the shelf-life of fruits and vegetables are volatile compounds, essential oils and, phenolic acids (Ayala Zavala et al., 2011).

- i. **Volatiles and essential oils:** Volatiles and essential oils are compounds that contribute to characteristic flavors and aromas of food products such as fruits, vegetables, herbs, spices etc. These are mainly comprised of terpenes, alcohols, aldehydes, ketones, terpenoids and apocarotenoids. Volatiles such as jasmonates have been used as elicitors as they play a key role in signal molecules in plant defence responses against biotic stress (microbial contamination). These also induce synthesis of antioxidants such as vitamin C and phenolic compounds (Solis et al., 2004). Similarly, essential oils are terpenes resistant to bacteria, pathogens, yeasts and fungi (Faleiro, 2011). It shows an antimicrobial activity. Friedman et al. (2004), showed that carvacrol, oregano, and cinnamaldehyde were effective antibacterial against antibiotic-resistant *Bacillus cereus*, *Campylobacter jejuni*, *E. coli*, *Salmonella enterica*, and *Staphylococcus aureus*. Its general hypothetical study explains essential oil targets the bacterial cell by disturbing the lipids of cell membrane and mitochondria, disrupting the flow of electrons and proton motive force, inhibition of protein synthesis and active transport, thus, rendering them permeable and leading to leakage of the cell contents (Afzaal et al, 2015). However, this treatment can affect the aroma and sensorial properties. Carvacrol and thymol have also demonstrated their potential to be used as active additives in PP films for food packaging applications by their controlled antimicrobial release to foodstuff and also by the possibility to protect food from degradation processes (Ramos et al., 2013).

Essential oils consist of cinnamon, cloves, garlic, oregano, rosemary and thyme which possess various inhibitory properties to stop the growth of spoilage or pathogenic bacteria, yeasts and molds. The essential oil containing thyme showed antagonistic effect against *Salmonella typhimurium* and *Staphylococcus aurus* (Juven and others 1994). Del campo et al. (2000), reported the minimum inhibitory concentration (MIC) exhibited by ethanolic solution containing rosemary extract showed effect of 1% on *Leuconostoc mesenteroides*, 0.5% for *Listeria monocytogenes*, 0.5% for *Staphylococcus aureus*, 0.13% for *Streptococcus mutans*, 0.06% for *Bacillus cereus* 5 and 1% for *Escherichia coli*. Another study stated the decrease in the sensitivity of *Bacillus cereus* towards carvacrol-after observing its growth in the presence of non-lethal carvacrol concentrations (Ultee and others 2000). Hence, the use of essential oils in films

or coatings shall become a valuable method to gain functional edible packaging with dual properties i.e. antioxidant and antibacterial activity.

- ii. **Phenolic compounds:** Phenolic compounds are ubiquitous constituents of higher plants found in a wide range of commonly consumed plant foods such as fruits, vegetables, cereals and legumes, and in beverages of plant origin, such as wine, tea and coffee (Cheynier, 2005). Flavanoids show excellent properties against microbial attack for fruits and vegetables (Lima et al., 2014). The proposed mechanism includes substrate complex formation, membrane disruption, enzyme inactivation and metal chelation (Holley and Patel, 2005). They are also used as edible coatings in meat products.
- iii. **Ethanol emitters:** Ethanol has been used as the antimicrobial agent for centuries. It prevents microbial spoilage of intermediate moisture foods and reduces the rate of staling and oxidative changes. It is known to reduce staling by acting as a plasticizer in the protein network of the bread. Ethanol as a food preservative is a novel application in the form of emitting sachet or film. A slow or rapid release of ethanol from the carrier material to the package headspace is regulated by permeability of the sachet material water vapour and ethanol. The sachets contain 55% ethanol and 10 % water which are absorbed onto silicone powder (35 %) and are filled with a paper-ethylene vinyl acetate copolymer sachet. Some sachets in addition to ethanol, may contain trace amounts of flavouring substances, such as vanilla or other flavors, to mask the alcohol odor in the package headspace. Certain ethanol emitters are dual action sachets which scavenge oxygen as well as emit ethanol vapor. Films containing ethanol are not so prevalent as compared to sachets because of issues in the controlled release of ethanol from the film into the package headspace. Ethanol embedded films usually requires additional layers in the film structure to retain ethanol and release it in a controlled manner; this increases the cost of the systems (Encyclopedia of food microbiology). Possible applications of ethanol emitters are bakery products and dried fish. Studies have shown that ethanol vapor generation is effective in controlling numerous species of molds, including Aspergillus and Penicillium; Bacteria inc Salmonella spp., Staphylococcus spp; yeasts such as Sachcharomyces cerevisiae. Commercial applications of ethanol emitters include Ethicap, Antimold and Negamold (Freund Industrial Co. Ltd, Japan), Ageless type SE (Mitsubishi Gas chem. Co.) etc.
- iv. **Flavour releasers or odor absorbers:** The presence of oxygen is a major factor in many spoilage mechanisms of food products that cause food deterioration, if found in a food package. Lipid oxidation is the main cause of flavor deterioration, off-flavors and off-odors oily foods such as peanuts. Lipid oxidation leads to oxidative rancidity, which is the most common cause of deterioration of oils in foods. Oxidative rancidity is associated with an unpleasant odor and flavor as a result of free radicals generated during the oxidation. During storage of packaged foods, microbial metabolites and protein breakdown products, such as amines and aldehydes, accumulate in the headspace of the package, leading to putrid (H_2S) and unpleasant odors. Moreover, physical characteristics of the packaging material (permeability, migration and scalping) may significantly affect the quality and safety of the product. Thus, there is a need to remove the undesirable odor causing constituents. These are added in the food packages to eliminate any malodours that may develop due to various chemical reactions taking place inside the package, such as bad odours from both, oxidative as well as nonoxidative biochemical spoilage. Also, the practice of incorporating fragrances and aromas into the packaging film suggests a good avenue for flavour emitting packaging. Gradual release of odors can offset the natural loss of taste or smell of products with long shelf lives (Almenar et al., 2009).

In order to increase the desirability and flavor of foods for consumers, to improve the aroma of fresh produce so as to increase its consumption and profitability, these flavor releasers and odor absorbers can prove to be beneficial. These flavors and aromas are released slowly and evenly in the packaged product during its storage, this release of flavors can also be regulated by use of controllers. Gradual release of odors can offset the natural loss of taste or smell of products with long shelf lives (Almenar et al 2009). For instance, an active packaging system to reduce the bitterness in bitter oranges is based on a thin cellulose triacetate or acetylated layer coated onto the inner surface of the plastic bottles acting as a limonene absorber. Also, the bitter component, naringenin, present in citrus juices, can be removed by binding the enzyme naringinase to the packaging material (Mexis and Kontominas, 2014). As a result, the juice tastes much sweeter and valued highly by the consumer. Sulfide scavengers have been effective in removing H₂S off flavors generated during the spoilage of poultry products (Mexis and Kontominas, 2014).

Presence of off odors within food packages is unacceptable. Therefore, addition of various odor removers/absorbers into packaging system is becoming increasingly important in some classes of food. Packaging of ready to eat meals, meat, fish, poultry and beverages use flavor releasers and odor absorbers. Recently a patent filed by US on an absorbent pad that contained activated carbon to reduce confinement odor in a vacuum-packaged food product. An embodiment of absorbent pad contained activated carbon and an antimicrobial agent that was found to reduce confinement odor by two mechanisms of action: first mechanism, reducing bacterial counts in the liquid purge that cause breakdown of carbohydrates and proteins in food products; second method is of trapping of confinement odor-causing breakdown products by the activated carbon (Sayandro et al., 2015).

NANOCOMPOSITES ACTIVE PACKAGING MATERIAL

There has been an increase use of polymer nanocomposites in the food packaging sector. The use of nanoparticles into polymers provides numerous benefits over other packaging systems such as improved mechanical, thermal and barrier properties. Due to the size of nanoparticles, a larger surface area is realized (Carbone et al, 2016). Hence, the interaction between the filler, matrix and the final performance of the film material is benefitted. However, there is also a risk that nanoparticles may migrate from the packaging material into the foodstuff during storage (Metak et al, 2015; Bumbudsanpharoke and Ko, 2015). Therefore, impacting the food safety of the product and the migration of nanomaterials can cause sensory changes (Huang et al, 2015).

PLA-Based Nanocomposite Active Packaging: The fundamental aim of active packaging is to extend shelf life and maintain or even improve the quality of food (Majid et al, 2016). Lorite et al (2017), studied the life cycle assessment of freshly cut melons. The packaging material was based on PLA enriched with nanoclays and surfactants. Reference material were original PLA and polyethylene terephthalate (PET). The food packaging materials were also analyzed under physiochemical and microbiological conditions. The results showed that the inclusion of nanoparticles improved the performance of the original PLA-based material. Although the production of the nanocomposite PLA materials requires more energy, it is eco-friendlier and has a lower impact on human health compared to the two reference materials.

Antimicrobial Nanoparticles: Recent advances in nanocomposites has become an important component in the active packaging area, especially for food applications (Ayhan 2013). Generally, the size of the nanoparticles used is between 1 and 100nm. Antimicrobial nanoparticles are fused into a polymer matrix with the aim of prolonging the shelf life of packaged food.

High surface-to-volume ratio and enhanced surface reactivity of the nanosized antimicrobial agents cause inactivation of microorganisms more effectively than their micro or macro-scale counterparts (Radusin et al, 2016). This type of packaging material is majorly dependent on the nature, size and specific area of the nanoparticles. The number of studies consisting of incorporation of antimicrobial nanoparticles in food systems are very less (Panea et al, 2014; Azlin-Hasim et al, 2016; Li et al, 2017).

EDIBLE COATINGS AS ACTIVE PACKAGING MATERIAL

An edible film or coating is a thin layer, which can be consumed, coated on a food to protect the product and used as a barrier between the food product and its environment (Cagri et al, 2004). These edible films and coatings, serve as a selective membrane for moisture transfer, oxygen and carbon uptake, lipid oxidation and losses of volatile aromas and flavors. Further, they improve mechanical handling properties, food quality and shelf life (Wang et al, 2013; Cagri et al, 2004; Olivas; Barbosa-Canovas 2005). It has been observed that the importance of edible films has become increasingly popular with respect to food protection and preservation due to the high demand of consumers for longer shelf-life and better quality of fresh foods as well as of environmentally friendly packaging (Park and Zhao 2004; Wang et al, 2014; Tharanathan 2003). Baldwin et al (1995), reported that the addition of emulsifiers (glycerol, Tween-20) reduced the superficial water activity and rate of 3 moisture loss in food products.

Furthermore, the edible films are broadly classified into three categories based on the nature of edible films and coatings. These are hydrocolloids (such as proteins, polysaccharides or alginates), lipids (such as by fatty acids, acylglycerols or waxes) and composites (made by combining substances from the two categories) (Krochta and DeMulderJohnston 1997; Donhowe and Fennema 1993). The advantages of edible films and coatings include (Debeaufort and others 1998; Mchugh and Krochta 1994; Dhall 2013; Dutta and others 2009), the source of edible films are from natural substances which ensures safety, their biodegradable nature reduces environmental pollution. High barrier and mechanical efficiencies inhibits the transmission of water, oil, and flavor components. It also provides suitable biochemical, physical, chemical and microbial stability in food products. It enhances the organoleptic, physical and nutritional properties of foods and provides individual protection of small pieces of foods. Edible films and coating requires basic technology and low cost of raw materials and processing.

The application of edible films and coatings are usually done with the incorporation of bactericidal agents or growth inhibitors into film or coating-forming materials to form antimicrobial films and coatings. This will retard surface growth of bacteria, yeasts and molds on a wide range of products (Coma et al, 2002; Cagri et al, 2004). The formation of such antimicrobial edible films and coatings serve as carriers for various antimicrobials that can extend shelf-life and reduce the risk of pathogen (Cagri et al, 2004). A natural polysaccharide produced by deacetylation of chitin in the presence of alkali is known as Chitosan. Elsabee and Abdou 2013a, observed that chitosan has the potential to act as a food preservative of natural origin on the basis of in vitro trials as well as through direct application on real complex matrix foods. These studies have provided proof that chitosan is an excellent film forming material. Further, chitosan films have a selective permeability to gasses, thereby delaying ripening and decreasing transpiration rates in fresh fruits and vegetables. Earlier studies done by Butler et al, 1996 on chitosan films showed stable mechanical and barrier properties during storage.

Edible films and coatings are thin continuous layers of edible material that have been researched upon extensively till date. Gomez-Estaca et al. (2014) suggested that its mechanism of action is the reduction of the oxygen transmission rate, as well as

the possibility of incorporating antioxidant compounds in the edible film or coating matrix; this vehicle has the advantage of close contact between coating and food. An edible film or coating does not act as a package itself, but it may reduce the barrier requirements of the package (Gomez Estaca et al., 2014). Edible film and coating technologies have been gaining prevalence in extending the shelf life of foods and has also been the subject of various reviews (Falguera et al., 2011; Rojas-Grau et al., 2009). In other words, edible coatings and films provides a vast array of advantages like biodegradability, edibility, good aesthetic appearance as well as barrier properties. Edible films and coatings protect the food constituents from any external physical, chemical and biological spoilage and thus, increase the shelf life as well as the quality of the food. They can also function as the carriers for food additives, including antimicrobials that can lessen the instances of food spoilage. (Cagri et al., 2004). These features, hence gives an added advantage over traditional packaging techniques.

Table 3: Various known active packaging systems and the substances used in them.

Type of active packaging system	Substances used and mode of action
Oxygen absorbing	Enzymatic systems (glucose oxidase-glucose, alcohol oxidase-ethanol vapor) Chemical systems (powdered iron oxide, catechol, ferrous carbonate, iron-sulfur, sulfite salt-copper sulfate, photosensitive dye oxidation, ascorbic acid oxidation, catalytic conversion of oxygen by platinum catalyst)
Carbon dioxide absorbing/ emitting	Iron powder-calcium hydroxide, ferrous carbonate- metal halide
Moisture absorbing	Silica gel, propylene glycol, polyvinyl alcohol, diatomaceous earth
Ethylene absorbing	Activated charcoal, silica gel-potassium permanganate, Kieselguhr, bentonite, Fuller's earth, silicon dioxide powder, zeolite, ozone
Ethanol emitting	Encapsulated ethanol
Antimicrobial releasing	Sorbates, benzoates, propionates, ethanol, ozone, peroxide, sulfur dioxide, antibiotics, silver-zeolite, quaternary ammonium salts
Antioxidant releasing	BHA, BHT, TBHQ, ascorbic acid, tocopherols
Flavor absorbing/Flavour releasing	Baking soda, active charcoal
Nanocomposites	Silver Nano particles and Titanium oxide (Ag/tio2), Nano-Silver and Zno
Edible coatings	benzoates, propionates, sorbates, parabens, Acidifying agents (acetic, lactic acid), curing agents (sodium chloride, sodium nitrites), bacteriocins (nisin, Lacticin), grape seed extracts, enzymes (peroxidase, Lysozyme), proteins.

ACTIVE PACKAGING: SAFETY CONCERNS

Novel food packaging techniques such as active packaging, is being developed at a great pace in response to consumer demands in order to provide them with fresh, wholesome, cost-effective and convenient, quality products at their doorstep. Unlike traditional food packaging techniques that provide limited benefits i.e. mainly preventing the interaction between the outside atmosphere and inside contents of the package, newer food packaging technologies have much more to offer. Due to deliberate changes made to the food and/or its environment, active packaging poses great challenge to the evaluation of safety of the product as compared to the traditional packaging. Such challenges include migration of undesirable components into the food, incorrect use of the packaging due to the insufficient labeling, less efficacy of active materials etc.

The challenges related to active packaging may be addressed by proper labeling with an intent to avoid its misuse and misunderstanding by the consumers. Also, compliance testing of migration of active materials to food using dedicated migration and toxicity investigations should be adapted, efficiency of the packaging w. r. t the functions the package has claimed must be checked. Nanotechnology is also expected to play a major role by taking into account various additional safety considerations (Dainelli et al, 2008).

CONCLUSION

Active packaging has a great scope in Asian as well as European countries due to increasing preferences for minimally processed and naturally preserved foods. However, the consumers are not very keen on the usage of sachets/pads in food packages due to fear of ingestion and the possibility of its leakage to food contents inside the package. The future trend of active packaging is to use the absorbing or releasing compounds incorporated in the packaging film or in an adhesive label to get rid of separate sachets in package, to prevent microbial spoilage, to increase the shelf life of food products and hence get consumer acceptance so that these absorbers/emitters are commercialized on a bigger scale. The group of scavengers seem to become popular in coming years. Lately, antioxidants and oxygen scavengers have been incorporated into packaging; tocopherols (Vitamin E) have gained prevalence and is thought to absorb malodours during plastic processing. More research is required on the safety issues regarding incorporation of carbon dioxide emitters/absorbers in the food package. Although, there have been many hurdles faced in the commercialization of some active packaging concepts but still these concepts are gaining high attention by researchers. Now, the commercially available active concepts include anti-fogging films, anti-sticking films, color containing films, light blocking/regulating systems, gas permeable/breathable films, insect repellent films etc. However, the legislative structure of Europe has restricted the commercial introduction of scavenging technologies. Active compounds need to be registered on positive lists and the overall and specific migration limit needs to be respected (Vermeiren et al. 2003). As legislative barriers initiate to disappear and more companies gradually become aware of the economic advantages of using this technology and thus consumers becoming more appreciative of this technological approach. Further researches on the designing, the interactions between food constituents and food package and their practical usage will definitely enhance consumer's faith in active packaging applications.

Active packaging has become the most accepted methods for extending the shelf life of perishable and semi-perishable products as it consists of various substances that can either absorb or release a specific gas or control the internal atmosphere of the package. Hence, the concept of active packaging plays an integral role in extending the shelf life and quality of the product. It is the system in which the product, the package and the environment interacts in the positive way.

Hence, the purpose of AP technologies for use in food industry is therefore to provide the aforementioned functionalities. Recently, a wide range of successful works have been done on the exploitation of AP systems for various food products packaging.

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