



ELSEVIER

Contents lists available at ScienceDirect

## Trends in Food Science &amp; Technology

journal homepage: www.elsevier.com



## Review

## A concise guide to active agents for active food packaging

Carla Vilela<sup>a, \*\*</sup>, Mia Kurek<sup>b</sup>, Zvi Hayouka<sup>c</sup>, Bettina Röcker<sup>d</sup>, Selçuk Yildirim<sup>d</sup>, Maria Dulce C. Antunes<sup>e</sup>, Julie Nilsen-Nygaard<sup>f</sup>, Marit Kvalvåg Pettersen<sup>f</sup>, Carmen S.R. Freire<sup>a, \*</sup>

<sup>a</sup> CICECO – Aveiro Institute of Materials, Department of Chemistry, University of Aveiro, 3810-193, Aveiro, Portugal

<sup>b</sup> Faculty of Food Technology and Biotechnology, Laboratory for Food Packaging, University of Zagreb, 10000, Zagreb, Croatia

<sup>c</sup> Institute of Biochemistry, Food Science and Nutrition, The Robert H. Smith Faculty of Agriculture, Food and Environment, The Hebrew University of Jerusalem, Rehovot, 76100, Israel

<sup>d</sup> Zurich University of Applied Sciences, Institute of Food and Beverage Innovation, Department of Life Sciences and Facility Management, 8820, Wädenswil, Switzerland

<sup>e</sup> CEOT/MeditBio, University of Algarve, FCT edf. 8, Campus de Gambelas, 8005-139, Faro, Portugal

<sup>f</sup> NOFIMA – Norwegian Institute of Food, Fisheries and Aquaculture Research, P.O. Box 210, NO-1431, Ås, Norway

## ARTICLE INFO

## Keywords:

Active agents  
Antimicrobial  
Carbon dioxide emitters  
Antioxidant  
Oxygen and ethylene scavengers  
Active food packaging

## ABSTRACT

**Background:** The ever-growing world population results in the ineluctable increase of food demand which translates in the augment of the global market of packaging materials. Hence, the concept of active packaging materializes as a technology to enhance the safety, quality and shelf-life of the packaged foods. Active packaging systems can contribute to the reduction of food waste by providing, apart from an inert barrier to external conditions, several functions associated with food preservation, namely absorbing/scavenging, releasing/emitting and removing properties, temperature, microbial and quality control.

**Scope and approach:** The purpose of this review is to present a concise (but wide-ranging) appraisal on the latest advances in active agents for active food packaging. Emphasis is placed on active functions such as antimicrobial and antioxidant activity, oxygen and ethylene scavenging, and carbon dioxide emitting. An effort was made to highlight representative articles that prompted research on active agents towards viable market solutions.

**Key findings and conclusions:** Active packaging is a thriving field given its duality as barrier to external detrimental factors and active role in food preservation and quality. The use of natural active agents is a flourishing field due to the general concern towards natural-based additives. Nevertheless, research is still in its early stages with a long way to go in the design of innovative and economical active packaging materials containing appropriate active agents. The interaction between packaging, environment and food is the key challenge for achieving commercial translation.

## 1. Introduction

The impressive surge of interest in the concept of active packaging is mainly driven by the ever-growing population and simultaneous increase of food demand and consumer trends. The inception of active packaging systems, *viz.* packages containing additives that maintain or extend product quality or shelf-life (Biji, Ravishankar, Mohan, & Gopal, 2015; Yildirim et al., 2018), is contributing vigorously to the reduction of spoilage, food waste, food recalls, and foodborne illness outbreaks. Additionally, the combination of active packaging with the concepts of intelligent and responsive packaging is the food packaging concept. The former aims at monitoring the condition of packaged food by giving in-

formation regarding the quality of the packaged food during transportation and storage, *e.g.*, indicators, data carriers and sensors (Ghani, Cozzolino, Castelli, & Farris, 2016), whereas the latter reacts to stimuli in the food or environment to enable real time food quality and food safety monitoring or remediation (Brockgreitens & Abbas, 2016). Although these technologies are largely used for food applications, they have also relevance for packaging of cosmetics, pharmaceuticals and other consumer goods products (Bastarrachea, Wong, Roman, Lin, & Goddard, 2015; Larson & Klivanov, 2013).

The use of active systems should comply with the requirements of different regulatory agencies, such as the Food and Drug Administration (USA), the European Food Safety Authority (European Union), or others, that set the legal basis for their accurate use, safety and market-

\* Corresponding author.

\*\* Corresponding author.

Email addresses: cvilela@ua.pt (C. Vilela); cfreire@ua.pt (C.S.R. Freire)

ing (Restuccia et al., 2010). Despite the huge popularity of active packaging in Japan introduced in the market in the mid-1970s (Restuccia et al., 2010), its use in Europe is only now beginning to increase. The high cost, low consumer acceptance and stringent legislation are the key points hindering the diffusion in the EU market of such systems, which are now being addressed by increasing the research and development (R&D) in the field and finding dissemination approaches for communicating the outcomes (Werner, Koontz, & Goddard, 2017). An illustrative example of these efforts includes the COST Action FP1405 (2014–2019) focused on the R&D of active and intelligent fibre-based packaging in terms of innovation and market introduction, as well as the Active & Intelligent Packaging Industry Association (AIPIA) with the aim of connecting the manufacturers, distributors, retailers and governmental agencies with products and services employing active and intelligent packaging technologies (Werner et al., 2017).

The wide diversity of active packaging systems comprise additives with a multitude of active functions, namely absorbing/scavenging properties (e.g., oxygen, carbon dioxide, ethylene, moisture, flavours, taints and UV light); releasing/emitting properties (e.g., ethanol, carbon dioxide, antioxidants, preservatives, sulphur dioxide and flavours); removing properties (catalysing food component removal: lactose, cholesterol); and temperature, microbial and quality control (Restuccia et al., 2010; Yildirim et al., 2018). These active packaging systems can be prepared by incorporation, coating, immobilization or surface modification onto the packaging materials (Bastarrachea et al., 2015), and the effect of such agents on the quality of different foods have been extensively reviewed by Yildirim et al. (2018). The commercialization stories in the food packaging sector are thriving with several companies already commercializing active packaging (Fig. 1) systems such as Biomaster® (silver based antimicrobial packing from Addmaster Limited, USA), Bioka (enzyme based O<sub>2</sub> scavenger from Bioka Ltd., Finland), Peakfresh (activated clay ethylene scavenger from Peakfresh Products Ltd., Australia), Dri-Loc® (moisture absorbent pad from Sealed Air Corporation, USA), FreshPax Type M® (CO<sub>2</sub> releaser from Multisorb Technologies Inc., USA), among others (Biji et al., 2015; Wyrwa & Barska, 2017). Additionally, the active agents used for active packaging are following the same trend as the packaging materials towards natural-based and eco-friendly alternatives (Kuswandi, 2017; Schumann & Schmid, 2018; Silva-Weiss, Ihl, Sobral, Gómez-Guillén, & Bifani, 2013; Valdés, Mellinas, Ramos, Garrigós, & Jiménez, 2014).

Numerous excellent reviews on food packaging systems with active features have been published recently, including the appraisals on innovative active, intelligent and bioactive food packaging technologies

(Majid, Nayik, Dar, & Nanda, 2017), active packaging applications for food (Yildirim et al., 2018), active edible films (Mellinas et al., 2016), active packaging coatings (Bastarrachea et al., 2015), natural additives for active food packaging (Silva-Weiss et al., 2013; Valdés et al., 2015, 2014), active packaging systems for muscle foods and dairy products (Ahmed et al., 2017; Haghghi-Manesh & Azizi, 2017), packaging concepts for fresh and processed meat (Schumann & Schmid, 2018), and EU regulation aspects and global market of active and intelligent food packaging (Restuccia et al., 2010), just to mention a few examples. Nonetheless, and to the best of our knowledge, there are no systematic reviews devoted solely to the active agents responsible for conferring the active functions to packaging materials. In this perspective, the present review attempts to illustrate the current trend in active agents for food packaging with focus on antimicrobial and antioxidant agents, oxygen and ethylene scavengers, and carbon dioxide emitters (Fig. 2). Although intelligent and responsive packaging represents a promising area of research (Brockgreitens & Abbas, 2016; Ghaani et al., 2016; Poyatos-Racionero, Ros-Lis, Vivancos, & Martínez-Mañez, 2018), it falls outside the scope of this review. Furthermore, a strenuous effort was made to select representative studies (published in the last 3 years) taking tangible steps towards viable solutions to enter the market.

## 2. Antimicrobial agents

Antimicrobial agents are one of the most studied active components since the growth of pathogenic and/or spoilage microorganisms are by far the major cause of food spoilage (Ahmed et al., 2017; Otoni, Espitia, Avena-Bustillos, & McHugh, 2016). Examples these microorganism include *Salmonella* spp., *Staphylococcus aureus*, *Listeria monocytogenes*, *Bacillus cereus*, *Escherichia coli* O157:H7 (pathogenic microorganisms); *Pseudomonas*, *Klebsiella*, *Lactobacillus* spp. (spoilage microorganisms bacteria); *Rhizopus*, *Aspergillus* (molds); and *Torulopsis*, *Candida* (yeasts) (Ahmed et al., 2017; Otoni et al., 2016). Therefore, antimicrobial agents are one of the active agent classes with the higher number of commercial products in the form of emitting sachets and absorbent pads (Otoni et al., 2016), such as Biomaster®, Aglon®, Irgaguard®, Surfacing®, IonPure®, Bactiblock®, Biomaster®, Food-touch®, Sanic Films, SANICO® and Wasaouro® (Realini & Marcos, 2014; Wyrwa & Barska, 2017). These examples of commercially available antimicrobial active packaging are mostly based on silver, silver zeolite, glucose oxidase, triclosan, chlorine dioxide, ethanol vapor emitting, natamycin, sulphur dioxide, and allyl isothiocyanate as active compounds (Fang, Zhao, Warner, & Johnson, 2017) for packaged meats, bread, cheese, fruit,

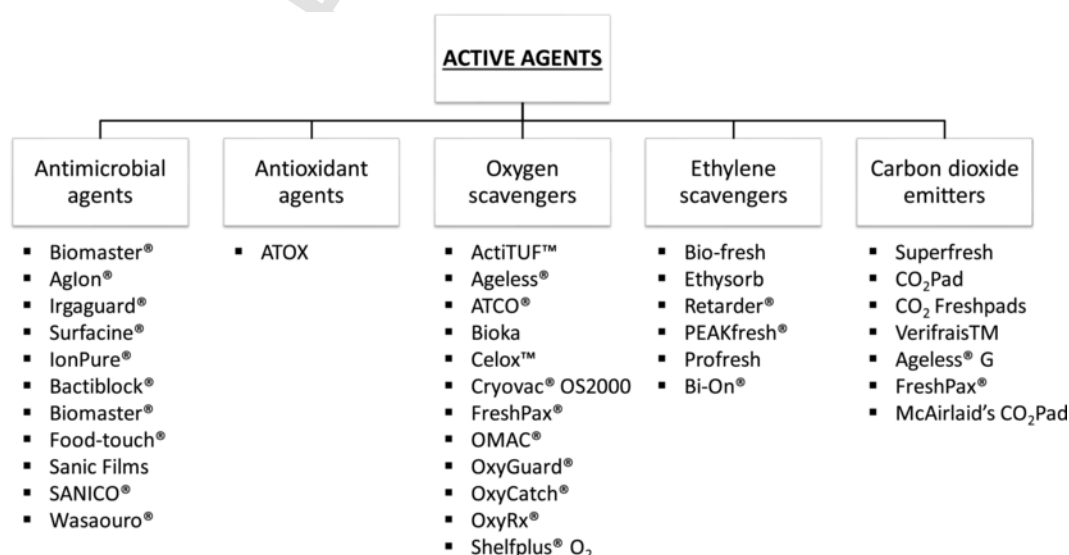


Fig. 1. Examples of commercial active agents for active food packaging.



Fig. 2. Active agents for active food packaging.

vegetables and dried fish products (Haghighi-Manesh & Azizi, 2017; Kapetanakou & Skandamis, 2016; Otoni et al., 2016; Yildirim et al., 2018). The absorbent pads are specially used in meat products since they can remove exuded liquid and in turn retard microbial growth (Otoni et al., 2016).

The list of scientific papers, reviews and books on the topic is extensive including a multitude of antimicrobial agents such as metal ions (e.g., silver, copper, gold and platinum), metal oxides (e.g.,  $\text{TiO}_2$ , ZnO and MgO), essential oils (e.g., thyme, oregano, pimento, clove, citron, lemon verbena, lemon balm and cypress leaf), plant extracts (e.g., grape seed, green tea, pomegranate peel/rind, acerola, pine bark, bearberry, cinnamon bark, rosemary, garlic, oregano, ginger and sage), polysaccharides (e.g. chitosan), pure bioactive components (e.g., thymol and carvacrol), peptides (e.g., nisin and lactoferrin), enzymes (e.g., peroxidase and lysozyme) and synthetic antimicrobial agents (e.g., quaternary ammonium salts, ethylenediaminetetraacetic acid (EDTA), and propionic, benzoic and sorbic acids) (Aziz & Karboune, 2018; Rhim, Park, & Ha, 2013). Therefore, the focus of the publications surveyed in the next paragraphs will be on the latest and most pertinent examples of antimicrobial systems dealing with metals, essential oils (EOs), biomacromolecules and combinations of more than one agent, as summarized in Table 1.

Various forms of metals have been used for their antimicrobial properties for thousands of years and are still among the most widely used antimicrobial agents. Out of all the metals with antimicrobial properties, silver and silver compounds, viz. metallic silver ( $\text{Ag}^0$ ), silver ions (most common  $\text{Ag}^+$ ) or silver nanoparticles (Ag NPs), were found to exert the most effective antimicrobial action against a broad range

of microorganisms at exceptionally low concentrations and present very little systemic toxicity toward humans (Dakal, Kumar, Majumdar, & Yadav, 2016). Other metals and metal-containing compounds like for example copper, gold, zinc oxide and titanium dioxide have also been found to display promising antimicrobial activity including in their nanoscale form. Further details regarding inorganic and metal nanoparticles and their antimicrobial activity in food packaging applications were broadly reviewed quite recently (Hoseinnejad, Jafari, & Katouzian, 2017). As a recent example, the study of Li et al. (2017) showed that the incorporation of ZnO nanoparticles into the poly (lactic acid) (PLA) matrix originated films with remarkable inhibition of microbial growth. In fact, ZnO nanoparticles were responsible for the reduction of the microbiological levels of bacterial, yeast and fungi counts in fresh-cut apple (Li et al., 2017).

Essential oils (EOs), viz. volatile aromatic mixtures composed of low molecular weight compounds (e.g. phenolic compounds, such as monoterpenes, flavonoids and phenolic acids) produced by plants (e.g., rosemary, clove, oregano, coriander, tea tree, lemongrass, basil, grape seed extract and fennel), or their isolated components (e.g., carvacrol, eugenol, thymol and cinnamaldehyde) have shown high efficacy in suppressing the growth of microorganisms and have been used as antimicrobial additives in active food packaging of cheese, fish, meat, fruits and vegetables (Maisanaba et al., 2017). EOs do not require extensive coverage here given the recently published reviews about their application as antimicrobial agents for active food packaging (Atarés & Chiralt, 2016; Maisanaba et al., 2017; Ribeiro-Santos, Andrade, Melo, & Sanches-Silva, 2017). The main drawback of EOs (and their components) is the need for high concentrations to achieve the same effectiveness in the real food, which could affect the organoleptic features of the food products. Furthermore, the mechanism of antimicrobial action of EOs is still unclear (Aziz & Karboune, 2018). Different combinations of polymer matrices and active compounds are possible (Atarés & Chiralt, 2016; Ribeiro-Santos et al., 2017; Severino et al., 2015; Yuan, Chen, & Li, 2016). As an example, gelatin composite films incorporated with clove essential oil and zinc oxide nanorods present a high antibacterial activity against *Listeria monocytogenes* and *Salmonella Typhimurium* inoculated in shrimp during refrigerated storage (Ejaz, Arfat, Mulla, & Ahmed, 2018). Another original contribution includes the study of Echeverría and co-workers about nanocomposite films based on soy protein isolate (SPI), montmorillonite (MMT) and clove essential oil for the preservation of muscle fillets of bluefin tuna (*Thunnus thynnus*) also during refrigerated storage (Echeverría, López-Caballero, Gómez-Guillén, Mauri, & Montero, 2018). These films promote a reduction of the final count of microorganisms until 12 days, and in the case of lactic bacteria and enterobacteria the counts remained near the detection limit throughout the storage (Echeverría et al., 2018).

In addition to metal-containing compounds and essential oils, biomacromolecules such as peptides (e.g., nisin and lactoferrin), enzymes (e.g., lysozyme) and polysaccharides (chitosan), are also being studied

Table 1  
Recent examples of antimicrobial agents incorporated into synthetic and bio-based polymer matrices.

| Antimicrobial agent                         | Film forming polymer      | Food product  | Microorganism   | Reference               |
|---|---------------------------|---|---|-------------------------|
| ZnO nanoparticles                           | PLA                       | Apple   | Bacterial, yeast and fungi  | Li et al., 2017         |
| Clove essential oil and zinc oxide nanorods | Gelatin                   | Shrimp  | <i>Listeria monocytogenes</i><br><i>Salmonella Typhimurium</i>        | Ejaz et al., 2018       |
| Clove essential oil                         | Soy protein isolate       | Muscle fillets of bluefin tuna ( <i>Thunnus thynnus</i> ) | <i>Pseudomonas</i> spp.<br>Lactic bacteria and enterobacterias counts | Echeverría et al., 2018 |
| Nisin                                       | PHB/PCL with organo-clays | Ham   | <i>Lactobacillus plantarum</i> CRL691                                 | Correa et al., 2017     |
| Lactoferrin                                 | Bacterial cellulose       | Fresh sausages  | <i>E. coli</i> <i>S. aureus</i>                                       | Padrão et al., 2016     |
| Lactoferrin and lysozyme                    | PET                       | Salmon  | $\text{H}_2\text{S}$ -producing bacteria                              | Rollini et al., 2016    |
| Lysozyme nanofibers                         | Pullulan                  | -   | <i>S. aureus</i>  | Silva et al., 2018      |
| Chitosan                                    | Chitosan                  | Pork slices   | Total viable counts (TVC)   | Wang et al., 2017       |

as active agents due to their well-recognized antimicrobial activity (Aziz & Karboune, 2018; Espitia et al., 2012). Nisin, the only bacteriocin peptide approved for food applications, is being used as a natural and safe food preservative in a variety of foods, including fruits, dairy products, dehydrated foods, poultry products and meat (Gharsallaoui, Joly, Oulahal, & Degraeve, 2016). This antimicrobial peptide is commercially known as nisaplin™ and has been shown to inactivate pathogens in fresh-cut watermelon, milk, skimmed milk powder, chicken and pork (Gharsallaoui et al., 2016). Recently, nisin activated polyhydroxybutyrate/polycaprolactone (PHB/PCL) nanocomposite films were tested against *Lactobacillus plantarum* CRL691 (used as processed meat spoilage bacterium model) inoculated on ham and the results confirmed the effectiveness of these films as shelf-life extender for vacuum-packed sliced cooked ham (Correa et al., 2017).

Lactoferrin, an iron-binding glycoprotein, is another peptide that exhibits antimicrobial activity against Gram-positive and Gram-negative bacteria, as well as fungi and parasites (Aziz & Karboune, 2018). Bacterial cellulose-lactoferrin edible films showed high antimicrobial activity against *E. coli* and *S. aureus* (Padrão et al., 2016). Furthermore, the edibility of the films was confirmed via *in vitro* gastrointestinal model for simulated digestion and the validity of these films as active food packaging materials was tested in fresh sausages as a model of meat products (Padrão et al., 2016).

Lysozyme, a peptidoglycan *N*-acetyl-muramoylhydrolase, is also known as a natural antimicrobial agent with activity against numerous pathogens (Aziz & Karboune, 2018). This single peptide enzyme is applied as food preservative due to its ability to hydrolyse the  $\beta$ -1,4-glycosidic linkages between *N*-acetylmuramic acid and *N*-acetylglucosamine found in peptidoglycan that compose the cell walls of Gram-positive bacteria. The same is not true for Gram-negative bacteria since lysozyme is prevented to access the peptidoglycan layer by the existence of a lipopolysaccharide layer surrounding the outer membrane of these microorganisms (Aziz & Karboune, 2018). Rollini et al. (2016) studied the performance of a poly (ethylene terephthalate)-coated film containing lysozyme and lactoferrin on the microbiological quality of fresh salmon. The combined use of lysozyme and lactoferrin made the films efficient in decreasing  $H_2S$ -producing bacteria at longer storage time and higher temperature (Rollini et al., 2016). Recently, the incorporation of lysozyme nanofibers into pullulan films endowed the multifunctional materials with antimicrobial activity against *S. aureus* (Silva, Vilela, Almeida, Marrucho, & Freire, 2018).

Chitosan, a cationic polysaccharide prepared via *N*-deacetylation of chitin, is by far the most studied polysaccharide in the context of food packaging due to its antimicrobial activity against a plethora of Gram-positive (e.g., *S. aureus*, *Listeria innocua* and lactic acid bacteria) and Gram-negative (e.g., *E. coli*, *Pseudomonas* spp. and *Salmonella* spp.) bacteria, and fungus (e.g., *Candida albicans* and *Aspergillus niger*) (Wang, Qian, & Ding, 2018). This polysaccharide was already combined with various agents, particularly with antioxidant additives, including quercetin (Souza et al., 2015), ellagic acid (Vilela et al., 2017), essential oils (Hafsa et al., 2016; Y.; Wang et al., 2017), among others. Chitosan's antimicrobial activity is generally associated with the amino group, but the mechanism of action is different in Gram-positive and in Gram-negative bacteria, as discussed in the recently published review about chitosan-based films for food packaging applications (Wang et al., 2018).

### 3. Carbon dioxide emitters

Carbon dioxide ( $CO_2$ ) is a gaseous molecule soluble in the aqueous and fat phases of food, resulting in the formation of carbonic acid and concomitant acidification of the food product. The beneficial antimicrobial properties of carbon dioxide are well known and extensively utilized in the food industry for quality preservation and shelf life extension.  $CO_2$  acts through a complex set of mechanisms, some of which remain to be fully understood, however are assumed to include an in-

terplay between e.g. alteration of the bacterial cell membrane, inhibition of bacterial enzymes and cytoplasmic pH changes. The joint action results in extension of the lag-phase and, thereby, growth inhibition of many spoilage bacteria (Sivertsvik, Jeksrud, & Rosnes, 2002; Yildirim et al., 2018).

In traditional modified atmosphere packaging (MAP) the ratio between the volume of headspace gas and food product, the g/p ratio, should optimally be 2/1 to 3/1 (Sivertsvik et al., 2002). This allows for high amounts of  $CO_2$  (high partial pressure) in the headspace, effective dissolution into the food product and reduced possibility of package deformation (due to  $CO_2$  absorption by the food product). However, high g/p ratios result in large package sizes and cause inefficient distribution, increased use of packaging materials and packaging gases and disadvantageous high environmental impact. Intuitively, at lowered g/p ratios, the  $CO_2$  amount in the headspace needs to be correspondingly higher to achieve an equivalent antimicrobial effect (Devlieghere & Debevere, 2000). However, package deformation due to under pressure formation would be pronounced without the continuous refill of  $CO_2$  in the package; an issue a  $CO_2$  emitter can accommodate. In the following the active agents and mechanisms for  $CO_2$  release for the most well-known and applied  $CO_2$  emitter technologies will be considered (Table 2). Furthermore,  $CO_2$  emitters in the form of sachets are mainly used for packaged vegetables, fresh meats and fish (Haghighi-Manesh & Azizi, 2017).

A commonly utilized  $CO_2$  releasing technology involves the active substances sodium bicarbonate ( $NaHCO_3$ ) and an organic acid. Citric acid is in many cases the acid of choice in such  $CO_2$  releasing systems (Yildirim et al., 2018). The reaction begins when liquid from the food product comes into contact with the active ingredients and dissolves them. The acid lowers the pH of the system to a value in which the sodium bicarbonate buffering system is shifted towards formation of un-dissociated carbonic acid and carbon dioxide according to Le Chatelier's principle. This implies that when liquid is introduced into the system, the pH will drop, and the production of carbon dioxide starts.

A commonly applied concept is enclosing sodium bicarbonate and citric acid dry powder at defined quantities and ratio into a liquid absorber pad. The pad is placed underneath the food product and functions as both a liquid absorber and a  $CO_2$  emitter, ensuring ease of use in production and often no need for additional steps in industrial packaging lines at implementation. A benefit of this  $CO_2$  emitter system is the flexibility in adjustment of the ratio between the active ingredients to give a pH compatible with the pH of a given food product, as performed in several published papers (Hansen, Moen, Rødbotten, Berget, & Pettersen, 2016; Holck, Pettersen, Moen, & Sørheim, 2014). The  $CO_2$  releasing system has been thoroughly studied in food systems, including in a few scientific publications documenting the effect of the emitter on quality, shelf life and MAP package sizes for cod (Hansen et al., 2016), reindeer meat (Pettersen, Hansen, & Mielnik, 2014) and chicken (Holck et al., 2014). The system is flexible, and the emitter capacity can be adjusted and optimized to the variable requirements of specific food products, such as physicochemical characteristics and size, as well as package volume, g/p ratios and gas compositions. Hansen and co-workers developed a model for calculation of required amounts of active agents for salmon fillets accounting for variables such as weight and surface area of the product, tray size and g/p ratio (Hansen, Høy, & Pettersen, 2009). Equivalent  $CO_2$  releasing systems can be found in which other organic acids act as the acidifier and reducing agent. The combination of the active ingredients sodium bicarbonate and ascorbic acid is an example of this (Yildirim et al., 2018). Ascorbic acid is known for its reducing properties and assumedly acts with dual function in this system, both as acidifier promoting  $CO_2$  formation and in addition as an  $O_2$  scavenger (Yildirim et al., 2018). The oxidation of ascorbic acid to dehydroascorbic acid consumes oxygen at a ratio of 1 mol  $O_2$  per 2 moles ascorbic acid (Cruz, Camilloto, & Pires, 2012). The antioxidant action of ascorbic acid may also be of benefit in packaging of food products with high fat contents, slowing down lipid ox-

Table 2

Recent examples of natural antioxidants, oxygen and ethylene scavengers, and carbon dioxide emitters incorporated into different matrices.

| Active agent                       | Matrix  | Food product                 | Reference                      |
|------------------------------------|---|------------------------------|--------------------------------|
| <i>Carbon dioxide emitter</i>      |   |                              |                                |
| Sodium bicarbonate and citric acid | Absorbent Pad Dri-Loc + MAP (60% CO <sub>2</sub> , 40% N <sub>2</sub> ) | Cod ( <i>Gadus morhua</i> )  | Hansen et al., 2016            |
| Sodium bicarbonate and citric acid | Sachet + MAP (100% CO <sub>2</sub> )                                    | Chicken                      | Holck et al., 2014             |
| Sodium bicarbonate and citric acid | + MAP (60% CO <sub>2</sub> , 40% N <sub>2</sub> )                       | Reindeer meat                | Pettersen et al., 2014         |
| <i>Antioxidant agent</i>           |   |                              |                                |
| Rosemary extract                   | Cassava starch  | Aqueous and fatty foods      | Piñeros-Hernandez et al., 2017 |
| Green tea extract                  | Hydroxypropyl-methylcellulose with PLA nanoparticles                    | –                            | Wrona et al., 2017             |
| Buriti oil                         | Chitosan  | –                            | Silva et al., 2016             |
| Ellagic acid                       | Chitosan  | –                            | Vilela et al., 2017            |
| Lysozyme nanofibers                | Pullulan  | –                            | Silva et al., 2018             |
| Acrylic acid (AA)                  | Polypropylene (PP)  | –                            | Lin, Decker, et al., 2016      |
|                                    |   | –                            | Tian et al., 2012, 2014        |
| Hydroxamic acid (HA)               | PP  | –                            | Lin, Decker, et al., 2016      |
|                                    |   | Liquid and semi-liquid foods | Roman et al., 2015             |
|                                    |   | –                            | Tian et al., 2013b             |
| HA                                 | Poly (ethylene terephthalate) (PET)                                     | –                            | Johnson et al., 2015           |
| Iminodiacetate (IDA)               | PP  | –                            | Lin, Decker, et al., 2016      |
|                                    |   | –                            | Lin & Goddard, 2018            |
| Polyphenol (catechin or catechol)  | PP  | –                            | Roman et al., 2016             |
| Lignin                             | Alginate  | –                            | Aadil et al., 2016             |
|                                    | Polyvinyl alcohol and chitosan  | –                            | Yang et al., 2016              |
| Naringin (and citrus extract)      | Chitosan  | –                            | Iturriaga et al., 2014         |
| Boric acid                         | Chitosan and gelatin  | –                            | Ahmed & Ikram, 2016            |
| Bixin                              | Cassava starch  | Sunflower oil                | Pagno et al., 2016             |
| $\alpha$ -Tocopherol               | Chitosan  | –                            | Martins et al., 2012           |
| Ellagic acid                       | Chitosan  | –                            | Vilela et al., 2017            |
| Mint and pomegranate peel extract  | Chitosan and poly (vinyl alcohol)                                       | –                            | Kanatt et al., 2012            |
| <i>Oxygen scavenger</i>            |   |                              |                                |
| Zero valent iron nanoparticles     | Silicon   | –                            | Folynowicz et al., 2017        |
| Palladium                          | PET/SiO <sub>x</sub>  | Ham                          | Yildirim et al., 2015          |
| Titanium oxide nanotubes           | –   | –                            | Tulsyan et al., 2017           |
| Ascorbic acid                      | –   | Meatloaves                   | Lee et al., 2018               |

Table 2 (Continued)

| Active agent  | Matrix   | Food product                  | Reference                    |
|---|--|-------------------------------|------------------------------|
| Pyrogallol  | LDPE   | Soybean oil                   | Gaikwad et al., 2017a, 2017b |
| Galic acid  | LDPE   | –                             | Ahn et al., 2016             |
| Galic acid  | Multilayered bio-based film  | –                             | Pant et al., 2017            |
| $\alpha$ -tocopherol                                    | PLA microparticles   | –                             | Scarfato et al., 2017        |
| $\alpha$ -tocopherol-loaded PCL nanoparticles           | Gelatin  | –                             | Byun et al., 2012            |
| Glucose oxidase   | Ethylene-vinyl acetate   | –                             | Wong et al., 2017            |
| Laccase   | Coated paper board, coated foil and free-standing films containing starch and different lignin derivatives | –                             | Johansson et al., 2014       |
| <i>Ethylene scavenger</i>                               |  |                               |                              |
| KMnO <sub>4</sub>                                       | Silica (SiO <sub>2</sub> ) and alumina (Al <sub>2</sub> O <sub>3</sub> ) nanoparticles                     | Tomato                        | Spricigo et al., 2017        |
| TiO <sub>2</sub> nanoparticles                          | Chitosan   | Cherry tomatoes               | Kaewklin et al., 2018        |
| Copper- and aluminium-based MOF                         | –  | Banana                        | Chopra et al., 2017          |
| Halloysite nanotubes (HNTs)                             | LDPE   | Banana, tomato and strawberry | Tas et al., 2017             |
| Palladium- and KMnO <sub>4</sub> -promoted nano-zeolite | –  | Tomato                        | Mansourbahmani et al., 2018  |

dation and development of rancid taste and odour causing quality deterioration (Yildirim et al., 2018).

Carbon dioxide releasing systems including the active agent ferrous carbonate (FeCO<sub>3</sub>) are briefly mentioned in a review paper (Restuccia et al., 2010). The reaction is assumed to be based on the solubility of such metal carbonates in acidic environments resulting in subsequent carbon dioxide release. However, little documentation of the reaction mechanism, requirements for other chemical components or current and potential applications of the technology can be found.

CO<sub>2</sub> emitters can also be composed of multiple different combinations of active agents. For instance, the combination of ascorbic acid and iron carbonate produces CO<sub>2</sub> and consumes O<sub>2</sub> at a 1:1 ratio (Hurme, Thea, & Nielsen, 2002). In a modelling study from 1999, the capacity of different combinations of reducing agents and carbonates was evaluated, seeking to find the optimal formulation and ratio between the ingredients for maximum O<sub>2</sub> uptake and CO<sub>2</sub> output. The study concluded that a combination of sodium ascorbate, sodium bicarbonate, sodium carbonate-10-hydrate and ferrous sulfate-7-hydrate made up the most efficient system (Huang, Hsu, & Chiang, 1999).

Commercial CO<sub>2</sub> emitter concepts based on different active ingredients exist on the market today. Still, in many cases documentation of the active components and the technology is scarce. Emitters based on sodium bicarbonate and citric acid includes Superfresh (Vartdal Plastindustri AS, Vartdal, Norway), CO<sub>2</sub>Pad (Cellcomb AB, Säfte, Sweden) and CO<sub>2</sub> Freshpads (CO<sub>2</sub> Technologies, Iowa, USA). The combination of sodium bicarbonate and ascorbic acid can be found in the Verifrais™ (SARL Codimer, Paris, France) CO<sub>2</sub> emitter (Kerry, 2014). Dual function systems of CO<sub>2</sub> emitters and O<sub>2</sub> scavengers based on either ferrous carbonate or a mixture of ascorbic acid and sodium bicarbonate in-

cludes Ageless<sup>®</sup> G (Mitsubishi Gas Chemical Co., Tokyo, Japan) and FreshPax<sup>®</sup> M (Multisorb Technologies Inc, New York, USA) (Coma, 2008). McAirmaid's CO<sub>2</sub>Pad is another concept on the market, however the combination of active ingredients is unknown (McAirmaid's Vliesstoffe GmbH, Berlingerode, Germany) (Yildirim et al., 2018).

#### 4. Antioxidant agents

Considerable interest has also been placed on antioxidant agents due to their ability to improve the stability of oxidation-sensitive food products. Oxidative degradation is, after microbial growth, the main reason of food spoilage (Gómez-Estaca, López-de-Dicastillo, Hernández-Munoz, Catalá, & Gavara, 2014) since oxidative reactions are responsible for (a) decreasing the nutritional value of food caused by the degradation of essential fatty acids, proteins and lipid soluble vitamins, (b) producing off-flavours and odours, and (c) colour change due to pigment degradation (Bastarrachea et al., 2015; Sanches-Silva et al., 2014). Two relevant reviews regarding antioxidant active packaging were published by Gómez-Estaca et al. (2014) and Sanches-Silva et al. (2014). The first reviewed the advances in antioxidant active packaging based on the incorporation of antioxidant agents in the package (Gómez-Estaca et al., 2014), whereas the second focussed on the natural antioxidants already applied in active food packaging (Sanches-Silva et al., 2014). A more recent review updated the information about edible and active films and coatings (based on cellulose derivatives, chitosan, alginate, galactomannans, gelatin, etc.) as carriers of natural antioxidants for lipid food (Ganiari, Choulitoudi, & Oreopoulou, 2017). The advantage of enclosing antioxidants within the packaging material surpasses the beneficial of their direct inclusion in food formulations. Therefore, most of the antioxidant systems are manufactured in the form of sachets, pads or labels, or incorporated into the packaging monolayer or multilayer materials (Gómez-Estaca et al., 2014; Sanches-Silva et al., 2014). ATOX is the trade name of a antioxidant packaging produced by the Spanish manufacturer Artibal, S.A., that consists in a film coating containing oregano essential oils for the protection of perishable foods (Realini & Marcos, 2014). Regarding foodstuffs, antioxidant agents are mostly used for packaged foods with high lipid content such as meat and fishery products, nuts, vegetable and fish oils (Ganiari et al., 2017).

A multitude of synthetic and natural antioxidant compounds are known to impart antioxidant activity to active packaging systems.

Therefore, a judicious selection should be carried out by considering the food characteristics as well as health and safety issues. The tendency is to move from synthetic antioxidants, namely butylated hydroxytoluene (BHT), butylated hydroxyanisole (BHA) and *tert*-butylhydroquinone (TBHQ), which are now suspected to be potentially harmful to human health (Nieva-Echevarría, Manzanos, Goicoechea, & Guillén, 2015), towards natural antioxidants with lower toxicity and higher safety (Ganiari et al., 2017; Pokorný, 2007; Sanches-Silva et al., 2014). Research on natural antioxidants as a detour to circumvent the safety issues associated with synthetic antioxidants is increasing with studies dealing with natural compounds (e.g., tocopherol, caffeic acid, carvacrol, quercetin, catechin, thymol, ferulic acid, carnosic acid and ascorbic acid), plant and fruit extracts (e.g., rosemary, grape seed, green tea, oregano, murta, mint, and pomegranate peel), and essential oils from herbs and spices (e.g., cinnamon, lemongrass, clove, thyme, ginger, oregano, pimento and bergamot) (Amorati, Foti, & Valgimigli, 2013; Ganiari et al., 2017; Sanches-Silva et al., 2014; Valdés et al., 2015). Nonetheless, the main drawback regarding the use of natural antioxidants is also the requirement for larger quantities to attain the same antioxidant activity in the food system (Tian, Decker, & Goddard, 2013a), as observed for antimicrobial activity of natural compounds-based systems.

Antioxidant compounds can be classified according to the mechanism of action as primary (or chain-breaking) antioxidants, namely free-radical scavengers, and secondary (or preventive) antioxidants including metal chelators, UV absorbers, singlet oxygen (<sup>1</sup>O<sub>2</sub>) quenchers and oxygen scavengers (Fig. 3), as reported in detail elsewhere (Islam, Khan, & Islam, 2017; Tian et al., 2013a). The advantage of secondary antioxidants lies in their capacity to reduce or prevent the occurrence of oxidation reactions, whereas the primary antioxidants react with free radicals to convert them into (fairly) stable products that do not engage in further initiation or propagation reactions. Worth noting is the fact that some active agents exhibit both mechanisms of action (Tian et al., 2013a). Moreover, the metal chelators, UV absorbers and <sup>1</sup>O<sub>2</sub> quenchers are emerging active agents for antioxidant active packaging systems but with recognized potential in other fields of application, as discussed by Tian et al. (2013a) in a review dedicated to the advances and emerging technologies in antioxidant active packaging with focus on maintaining quality and nutrition of packaged foodstuffs. Herein, all classes of antioxidants that contribute to reduce or avoid oxidative degradation reactions will be briefly discussed in terms of the

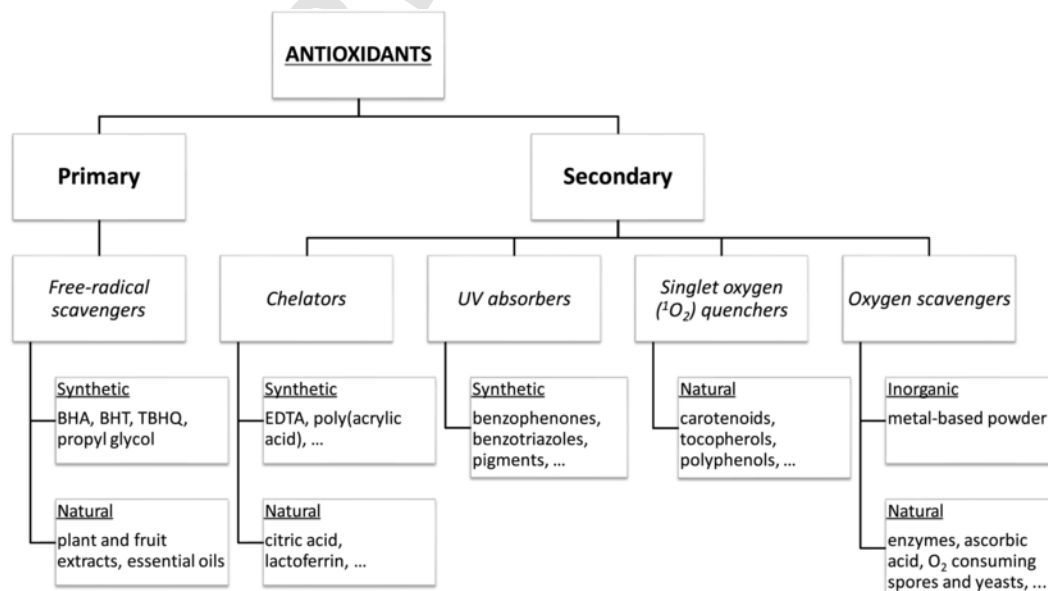


Fig. 3. Classification of antioxidant compounds based on their mechanism of action (Tian et al., 2013a).



latest relevant advances (Table 2), except for oxygen scavengers that will be covered in the following section since they are among the most widely used commercial active packaging technology.

Free-radical scavengers are certainly the most studied class of antioxidants that can donate hydrogen to reactive free radicals and form stable free radicals unable to perpetrate initiation or propagation reactions (Tian et al., 2013a). Examples of free-radical scavengers comprise the synthetic agents: BHA (E-320), BHT (E-321), TBHQ (E-319), propyl gallate (E-311), *etc.*, as well as the natural antioxidants: plant extracts, tocopherols and essential oils (Sanches-Silva et al., 2014; Tian et al., 2013a). As evoked above, the studies dealing with synthetic antioxidants are declining due to the increasing trend to avoid or minimize the use of adverse artificial food additives. Despite the ongoing research on the topic, most of the studies use synthetic antioxidants mainly for comparison purposes (Ashwar et al., 2015; Jamshidian, Tehrani, & Desobry, 2013; Nisa et al., 2015; Xia & Rubino, 2016). Regarding naturally occurring antioxidants only very recent contributions are discussed here due to thorough reviews available elsewhere (Islam et al., 2017; Maisanaba et al., 2017; Sanches-Silva et al., 2014). Some of the newly published research includes the study on edible cassava starch films containing polyphenols-rich rosemary extracts for aqueous and fatty foods (Piñeros-Hernandez, Medina-Jaramillo, López-Córdoba, & Goyanes, 2017), hydroxypropyl-methylcellulose films containing PLA nanoparticles loaded with green tea extract for food products with high fat content (Wrona, Cran, Nerín, & Bigger, 2017), chitosan films containing buriti oil (Silva, Lopes, Da Silva, & Yoshida, 2016) or ellagic acid (Vilela et al., 2017), pullulan films containing proteins nanofibers (Silva et al., 2018), among others.

In addition to primary antioxidants that react directly with lipid radicals and convert them into (fairly) stable products, secondary additives such as chelating agents, ultraviolet absorbers and singlet oxygen quenchers are also used in active packaging to reduce the rate of oxidation. Metal chelators convert metal pro-oxidants (*e.g.*, iron or copper derivatives) into stable products and comprise synthetic antioxidants, such as ethylenediaminetetraacetic acid (EDTA) and poly (acrylic acid) (PAA), but also natural antioxidants like for example citric acid and lactoferrin (Tian et al., 2013a). Recent publications covering the use of chelators as active agent in antioxidant active packaging materials mainly report the grafting of for example: (i) acrylic acid (AA) from a polypropylene (PP) surface, *i.e.* PP-g-PAA (Lin, Decker, & Goddard, 2016; Tian, Decker, & Goddard, 2012; Tian, Decker, McClements, & Goddard, 2014), (ii) hydroxamic acids (HA) from a PP surface, *i.e.* PP-g-PHA (Lin, Decker, et al., 2016; Roman, Decker, & Goddard, 2015; Tian, Decker, & Goddard, 2013b) or from a poly (ethylene terephthalate) (PET) surface, *i.e.* PET-g-PHA (Johnson, Tian, Roman, Decker, & Goddard, 2015), and (iii) iminodiacetate (IDA) and its derivatives from a PP surface, *i.e.* PP-g-IDA (Lin, Roman, Decker, & Goddard, 2016) and PP-g-PIDA (Lin & Goddard, 2018). In a different approach, PP films coated with polyphenols (catechin or catechol) can also be prepared with a metal chelating capacity of  $39.3 \pm 2.5 \text{ nmol Fe}^{3+} \text{ cm}^{-2}$  (Roman, Decker, & Goddard, 2016).

Ultraviolet absorbers constitute a class of light stabilizers capable of absorbing UV radiation and, thus, prevent photo-oxidation of light-sensitive foods such as ham and drinks. Benzophenones, benzotriazoles and pigments (*e.g.*, phtalocyanine,  $\text{TiO}_2$ ) are some examples of UV absorbers (Tian et al., 2013a). Recent contributions include the studies dealing with UV absorbers like for example: lignin (Aadil, Prajapati, & Jha, 2016; Yang et al., 2016), naringin (Iturriaga, Olabarrieta, Castellán, Gardrat, & Coma, 2014), boric acid (Ahmed & Ikram, 2016), bixin (Pagno, de Farias, Costa, Rios, & Flôres, 2016),  $\alpha$ -tocopherol (Martins, Cerqueira, & Vicente, 2012), ellagic acid (Vilela et al., 2017), and natural extracts rich in phenolic compounds (Kanatt, Rao, Chawla, & Sharma, 2012).

Research on singlet oxygen ( $^1\text{O}_2$ ) quenchers, although scarce, is mostly focussed on the use of natural active agents, such as carotenoids ( $\beta$ -carotene, lycopene, lutein, *etc.*), tocopherols and polyphenols (cate-

chins, flavonoids, *etc.*), that have the ability to deplete the excess energy of singlet oxygen and prevent photo-oxidation (Tian et al., 2013a).

## 5. Oxygen scavengers

A wide range of food products are sensitive to oxygen, therefore, the presence of residual headspace oxygen on packaged foods can negatively influence the quality and shelf-life by allowing the growth of aerobic microorganisms or oxidation of the product, which results in sensorial, colour or nutritional changes (Yildirim et al., 2018). Consequently, the food industry aims to exclude oxygen from food packaging, which is mainly performed by gas flushing or modified atmosphere packaging (MAP) processes, or more efficiently by using oxygen scavengers (OS) that control residual oxygen. ActiTUF<sup>TM</sup>, Ageless<sup>®</sup>, ATCO<sup>®</sup>, Bioka, Celox<sup>TM</sup>, Cryovac<sup>®</sup> OS2000, Enzyme-based FreshMax<sup>®</sup>, FreshPax<sup>®</sup>, OMAC<sup>®</sup>, OxyGuard<sup>®</sup>, OxyCatch<sup>®</sup>, OxyRx<sup>®</sup> and Shelfplus<sup>®</sup> O<sub>2</sub> (Realini & Marcos, 2014; Wyrwa & Barska, 2017) are examples of commercial products with oxygen scavenger technology. In terms of food products, OS are mainly utilized in packaged bread, cakes, pizza, pasta, cheese, cured meats and fish, coffee, beer, sauces and beverages (Haghighi-Manesh & Azizi, 2017).

The oxidative mode of action differs from technology to technology depending on the active compounds applied. Examples of OS-systems include iron, other metals (*e.g.*, cobalt, palladium, platinum), organic acids (*e.g.*, ascorbic and gallic acids), photosensitive dyes (*e.g.*, eosin, curcumin), unsaturated hydrocarbon dienes, enzymes and bacterial spores or yeasts (Yildirim et al., 2018). The majority of commercially applied OS are iron-based sachets and generally consist of a permeable sachet containing iron powder, whose moisture activated mechanism of action is based on the principle of iron oxidation (Arvanitoyannis & Oikonomou, 2012; Cooksey, 2010).

For a wide range of food applications, the performance of iron-based OS-sachets might have been sufficient, although sachet-based applications come along with drawbacks, namely the risk of accidental rupture leading to involuntary content consumption, the requirement of an additional packaging operation step, the inadequacy for beverages, and the inserts aesthetics differ from country to country. These constraints can be circumvented by developing alternative solutions using polymeric packaging films or containers as matrices for OS incorporation (Yildirim et al., 2018). Within the existing OS technologies, the use of iron nanoparticles, palladium, titanium oxide nanotubes, ascorbic acid, phenolic compounds (*e.g.*, pyrogallol, gallic acid and  $\alpha$ -tocopherol) and enzymes as active agents in polymeric matrices (*e.g.*, silicon, PET, low-density polyethylene (LDPE), PLA) applied to food products will be the ones exemplified here (Table 2).

An interesting publication regarding alternative OS-systems include the recent study about nanoscale oxygen scavengers based on zero valent iron particles with a silicone matrix (Folynowicz, Bardenshtein, Sangerlaub, Antvorskov, & Kozak, 2017). These nanoscale iron particles exhibited an OS-rate at least ten times higher at 100% relative humidity compared to commercially available iron-based OS incorporated in polyethylene or polypropylene polymer matrices (Folynowicz et al., 2017).

In a different study with a distinct active agent, a fast OS-system was developed by depositing palladium on a PET/SiO<sub>x</sub> film using magnetron sputtering technology (Yildirim, Rocker, Ruegg, & Lohwasser, 2015). This Pd-based OS-system successfully prevented discoloration of an oxygen-sensitive food such as cooked cured ham (Hutter, Ruegg, & Yildirim, 2016). Actually, this catalytic system based on palladium (with a high oxygen scavenging activity) was able to remove 2 vol% of the headspace oxygen concentration within 35 min, and no discoloration was detected for 21 days of storage at 4 °C under illumination (Hutter et al., 2016). Nevertheless, this catalytic system has the drawback of being susceptible to poisoning (inactivation) by volatile sulphur compounds present in the headspace of packaged food such as

roast beef, cheese, ham, peanuts and par-baked buns (Röcker, Rüeegg, Glöss, Yeretzyan, & Yildirim, 2017).

Another exciting development was recently reported by Tulsyan, Richter, and Diaz (2017) regarding an OS-system based on titanium oxide nanotubes (TONT). This TONT scavenger displayed oxygen uptake rates of up to three orders of magnitude higher than commercially available iron-based scavengers (Close, Tulsyan, Diaz, Weinstein, & Richter, 2015). Contrary to the previous OS-systems whose mechanism of action is moisture activated, these TONT scavengers have a high performance in dry conditions. Furthermore, their colour change in the presence of oxygen, from dark blue to a yellowish brown, associated with the reduction and oxygen uptake of TONT make them suitable as oxygen indicators to tamper-proof highly oxygen-sensitive product packaging (Tulsyan et al., 2017).

Recently, Lee and co-workers developed a non-metallic OS system based on activated carbon and sodium L-ascorbate with an oxygen-scavenging volume ca. 2.2 times higher than those of commercially available iron powder-containing OS (Lee et al., 2018). Additionally, the application of these ascorbic acid-based OS-systems during the storage of raw meatloaves confirmed their concomitant potential to inhibited lipid oxidation and reduced microbial growth of lactic acid bacteria, yeasts and molds (Lee et al., 2018).

Other original contributions include the studies of Gaikwad and co-workers about LDPE films containing a non-metallic OS technology based on pyrogallol, viz. a phenolic compound with high oxygen scavenging ability in alkaline medium (Gaikwad, Singh, & Lee, 2017a, 2017b). These LDPE/pyrogallol films presented significant oxygen scavenging capacity (0.816 mL O<sub>2</sub> per cm<sup>2</sup> after 8 days) under high humidity (75%) and temperature (60 °C) storage conditions (Gaikwad, Singh, & Lee, 2017b). Therefore, the films were tested for the packaging of soybean oil and the results confirmed the stability of the oil samples packaged with LDPE/pyrogallol films (Gaikwad et al., 2017a).

Gallic acid has also been used as a moisture-activated oxygen scavenger agent incorporated into LDPE films (Ahn, Gaikwad, & Lee, 2016). According to this study, the LDPE film containing 20% of gallic acid reached an oxygen scavenging value of 0.709 mL.cm<sup>-2</sup> over 7 days, which is in the range of commercial oxygen scavenging films. This phenolic compound was also incorporated into a multi-layered bio-based film (bio-LDPE and PLA) for the packaging of foodstuffs with high water activity (Pant, Sangerlaub, & Muller, 2017).

In another study, a fully biodegradable OS-system based on  $\alpha$ -tocopherol-loaded PLA microparticles was prepared with high encapsulation efficiency (Scarfato, Avallone, Galdi, Di Maio, & Incarnato, 2017). In terms of scavenging capacity and rate, the results are in line with the values required for an effective oxygen scavenger system. Similarly,  $\alpha$ -tocopherol was also loaded into PCL nanoparticles that were then incorporated into warm-water fish gelatin films with an oxygen scavenging capacity (moisture-activated) of 1969 cc O<sub>2</sub>/m<sup>2</sup>/mil thickness (Byun, Bae, & Whiteside, 2012). Nevertheless, the behaviour of both OS-systems was not tested in the presence of any real foodstuff.

These ongoing studies have been recently enriched by the study describing the fabrication of an enzymatic oxygen scavenging polymer coating prepared by hydrophobic modification of glucose oxidase (Wong, Andler, Lincoln, Goddard, & Talbert, 2017). This enzyme-catalysed OS was blended with ethylene-vinyl acetate and then casted onto the interior of glass vials to validate their potential as a commercially translatable coating method for enzyme immobilization. A few years earlier, Johansson, Gillgren, Winstrand, Järnström, and Jönsson (2014) also developed an enzyme-catalysed oxygen scavenger system, but this one was based on the laccase-catalysed oxidation of lignin derivatives in solid media. Several coatings and films, namely coated paper board, coated foil and free-standing films containing starch and different lignin derivatives, were tested regarding their oxygen scavenging ability (Johansson et al., 2014). Although the oxygen-scavenging results of both studies seem promising, they fail to validate the efficiency of the OS-systems in the presence of food products.

Combinations of OS technologies with other active agents (e.g. antimicrobial) are also common like for instance the recent study regarding the combined use of the commercial Ageless® OS iron-based sachet (i.e. one of the first developed sachets (Otoni et al., 2016)) with ginger essential oil as antimicrobial agent in a plastic pouch of multi-layer film of ethylene-vinyl alcohol (Remya, Mohan, Venkateshwarlu, Sivaraman, & Ravishankar, 2017). This combination aimed at extending the shelf-life of fresh cobia fish steaks stored at 2 °C. The results pointed to a packaging system capable of reducing and maintaining the concentration of oxygen inside the package to less than 0.01% during chilled storage, as well as to reduce the growth of aerobic *Pseudomonas* spp. and inhibit the bacterial growth of lactic acid bacteria and *Brochothrix thermosphacta* (Remya et al., 2017).

## 6. Ethylene scavengers

Ethylene (C<sub>2</sub>H<sub>4</sub>) is a small volatile molecule that acts as a phytohormone responsible for the ripening and senescence of fruits and vegetables (Álvarez-Hernández et al., 2018). Therefore, the post-harvesting control of ethylene levels in the atmosphere surrounding fresh food products during shipping, storage and handling is of major importance to enhance their quality and extend shelf-life. The most widely used ethylene scavengers are based on potassium permanganate (KMnO<sub>4</sub>) supported on inert matrices (e.g., silica gel or alumina), which oxidizes ethylene with a colour change from purple to brown. For instance, Spricigo, Foschini, Ribeiro, Corrêa, and Ferreira (2017) developed a nanostructured platform based on silica (SiO<sub>2</sub>) and alumina (Al<sub>2</sub>O<sub>3</sub>) nanoparticles impregnated with KMnO<sub>4</sub> that took advantage of this colour change to indicate ethylene removal (Spricigo et al., 2017). In fact, this inorganic compound has a great potential as ethylene absorber sachets during storage of, for example, different cultivars of tomatoes under refrigerated conditions (similar to those used by consumers at home) (Köstekli et al., 2016). Nevertheless, KMnO<sub>4</sub> cannot be used in direct contact with foodstuffs given its high toxicity and has a limited long-term efficacy in high-moisture environments (Yildirim et al., 2018; Álvarez-Hernández et al., 2018).

Alternative systems for ethylene elimination includes metal oxides (e.g., silica gel and activated alumina), layer silicates and zeolites (e.g., clays, vermiculite, zeolite), nanoparticles and activated carbon (Yildirim et al., 2018; Álvarez-Hernández et al., 2018) that can be incorporated into the package material or provided in sachets to be introduced into packages or storage environments. Numerous options are commercially available, namely Bio-fresh, Ethylene Control Power Pellet, Ethsorb®, EvertFresh Green Bags®, Retarder®, PEAKfresh®, Profresh and Bi-On® (Wyrwa & Barska, 2017; Yildirim et al., 2018; Álvarez-Hernández et al., 2018). Several papers have been published about ethylene scavengers in the domain of active food packaging (Table 2). Interesting results were obtained, for example, by Kaewklin et al. regarding chitosan films containing nanosized titanium dioxide (TiO<sub>2</sub>) to maintain quality and extend storage life of cherry tomatoes (Kaewklin, Siripatrawan, Suwanagul, & Lee, 2018). The authors claim this is the first study dealing with the application of chitosan and TiO<sub>2</sub> nanocomposite films as an ethylene scavenger for postharvest handling of a climacteric fruit. These films exhibited ethylene photodegradation which might contribute to delay the ripening process and extend the storage life of the most widely consumed vegetable crop (Kaewklin et al., 2018). In a different study, Chopra and co-workers tested metal organic frameworks (MOFs) as ethylene scavengers (Chopra, Dhupal, Abeli, Beaudry, & Almenar, 2017). The proof-of concept performed with banana fruits showed that copper- (Basolite C300) and aluminium-based MOF (Basolite A520) have the potential to sorb, store and release gaseous compounds that impact plant physiology, such as ethylene and 1-methylcyclopropene (1-MCP), i.e. an ethylene action inhibitor (Chopra et al., 2017). In another recent study, Tas et al. (2017) reported the preparation of LDPE nanocomposite films containing halloysite nanotubes (HNTs), i.e. hollow tubular clay nanoparticles. The



use of HNTs with high ethylene adsorption capacity slowed down the processes of softening and aging of banana, tomato and strawberry (Tas et al., 2017). As a last and noteworthy contribution, the efficiency of several ethylene scavengers, namely palladium-promoted nano-zeolite, KMnO<sub>4</sub>-promoted nano-zeolite, 1-MCP, CaCl<sub>2</sub>, salicylic acid and UV-C, on the maintenance of postharvest quality of tomato fruit was recently evaluated (Mansourbahmani, Ghareyazie, Zarinnia, Kalatejari, & Mohammadi, 2018). According to this study, palladium-promoted nano-zeolite is the tool that contributes simultaneously to self-life extension and preservation of quality characteristics of tomato fruits during storage (Mansourbahmani et al., 2018). Supplementary details regarding the current scenario in ethylene scavenging systems to extend fruit and vegetable postharvest life are available elsewhere (Zhang, Cheng, Wang, Khan, & Ni, 2017; Álvarez-Hernández et al., 2018).

## 7. Concluding remarks and future trends

Within the combined contexts of the ever-growing population and concomitant augment of food demand, it is not unexpected to witness a growing research effort in the field of active packaging, as in fact corroborated by the vast catalogue of publications portrayed in the present review. Therefore, this appraisal ventured into the advances in active agents for food packaging with special emphasis on antimicrobial and antioxidant agents, oxygen and ethylene scavengers, and carbon dioxide emitters, as illustrated in Fig. 1.

The key factors in developing active packaging systems should include the characteristics of the food (e.g., pH, water activity, nutritional components), and the activity, stability, migration and toxicity of the active agents, whose combination will improve shelf-life, safety and quality of food products. The major hurdle for active packaging is indubitably to design active materials capable of preserving their original mechanical and barrier properties, and simultaneously ensuring the activity of the active agents during the entire process of shipping, storage and handling as food packaging materials. Further key obstacles include technology transfer, manufacturing process scale-up, regulatory requirements for safety, environmental concerns, and consumer acceptance as discussed in a recent review about the “Hurdles to commercial translation of next generation active food packaging technologies” (Werner et al., 2017).

Consumers' demands and industry trends point to the increase of biodegradable and edible (e.g., polysaccharides and proteins (Ganiari et al., 2017)) packaging materials with natural derived active agents (Silva-Weiss et al., 2013; Valdés et al., 2015, 2014), contributing to diminish food waste and the environmental impact of packages, along with the augment of food safety and consumer health. Furthermore, the formation of trade associations (e.g., AIPIA) to connect food companies with packaging suppliers, and to foment of the partnerships between them and research entities will contribute to overcome the barriers to commercialization (Werner et al., 2017). Several companies are already commercializing active packaging systems in the form of sachets and pads, or films and coatings with active functions such as antimicrobial and antioxidant agents, oxygen and ethylene scavengers, and carbon dioxide emitters. Moreover, combinations of more than one agent are also being used for foodstuff requiring more than one active function to enhance their safety, quality and shelf-life. The active agents vary depending on the food characteristics with, for instance, antioxidant agents being quite relevant for lipid food products (Ganiari et al., 2017; Tian et al., 2013a), and ethylene scavengers for fruits and vegetables (Álvarez-Hernández et al., 2018).

One detail that should be mentioned about the published literature is the fact that most of the studies dealing with active agents are focused on the active properties of the enriched packaging materials, rather than testing their behaviour in the presence of real food products, thus failing to validate the efficiency of the active packaging system. Nevertheless, the studies that carry out proof-of-concept experi-

ments are mainly focussed on foodstuffs such as meat (Ahmed et al., 2017; Fang et al., 2017; Islam et al., 2017; Schumann & Schmid, 2018) and dairy (Haghighi-Manesh & Azizi, 2017) products, as well as fruits and vegetables (Aziz & Karboune, 2018; Álvarez-Hernández et al., 2018). Despite the extent and diversity of the research activities carried out in the last couple of years, not all these systems will reach viable practical realisations. Nevertheless, the relevancy of this topic will continue to draw increased attention from academia and industry.

## Acknowledgments

This work was developed within the scope of the project CICECO – Aveiro Institute of Materials, POCI-01-0145-FEDER-007679 (FCT Ref. UID/CTM/50011/2013), financed by national funds through the FCT/MEC and when appropriate co-financed by FEDER under the PT2020 Partnership Agreement. gs3:Fundação para a Ciência e a Tecnologia is acknowledged for a post-doctoral grant to C. Vilela (SFRH/BPD/84168/2012) and a contract under Investigador FCT to C.S.R. Freire (IF/01407/2012). The FPS COST Action FP1405: Active and intelligent fibre-based packaging – innovation and market introduction (ActInPak) is also acknowledged for promoting the collaboration between the authors.

## References

- Aadil, K.R., Prajapati, D., Jha, H., 2016. Improvement of physico-chemical and functional properties of alginate film by Acacia lignin. *Food Packaging and Shelf Life* 10, 25–33 <https://doi.org/10.1016/j.fpsl.2016.09.002>.
- Ahmed, S., Ikram, S., 2016. Chitosan and gelatin based biodegradable packaging films with UV-light protection. *Journal of Photochemistry and Photobiology B: Biology* 163, 115–124 <https://doi.org/10.1016/j.jphotobiol.2016.08.023>.
- Ahmed, I., Lin, H., Zou, L., Brody, A.L., Li, Z., Qazi, I.M., et al., 2017. A comprehensive review on the application of active packaging technologies to muscle foods. *Food Control* 82, 163–178 <https://doi.org/10.1016/j.foodcont.2017.06.009>.
- Ahn, B.J., Gaikwad, K.K., Lee, Y.S., 2016. Characterization and properties of LDPE film with gallic-acid-based oxygen scavenging system useful as a functional packaging material. *Journal of Applied Polymer Science* 133, 44138 <https://doi.org/10.1002/app.44138>.
- Álvarez-Hernández, M.H., Artés-Hernández, F., Ávalos-Belmontes, F., Castillo-Campohermoso, M.A., Contreras-Esquivel, J.C., Ventura-Sobrevilla, J.M., et al., 2018. Current scenario of adsorbent materials used in ethylene scavenging systems to extend fruit and vegetable postharvest life. *Food and Bioprocess Technology* 11 (3), 511–525 <https://doi.org/10.1007/s11947-018-2076-7>.
- Amorati, R., Foti, M.C., Valgimigli, L., 2013. Antioxidant activity of essential oils. *Journal of Agricultural and Food Chemistry* 61, 10835–10847 <https://doi.org/10.1021/jf403496k>.
- Arvanitoyannis, I.S., Oikonomou, G., 2012. Active and intelligent packaging. In: Arvanitoyannis, I.S. (Ed.), *Modified atmosphere and active packaging technologies*. CRC Press, Boca Raton, pp. 628–654.
- Ashwar, B.A., Shah, A., Gani, A., Shah, U., Gani, A., Wani, I.A., et al., 2015. Rice starch active packaging films loaded with antioxidants-development and characterization. *Starch* 67 (3–4), 294–302 <https://doi.org/10.1002/star.201400193>.
- Atarés, L., Chiralt, A., 2016. Essential oils as additives in biodegradable films and coatings for active food packaging. *Trends in Food Science & Technology* 48, 51–62 <https://doi.org/10.1016/j.tifs.2015.12.001>.
- Aziz, M., Karboune, S., 2018. Natural antimicrobial/antioxidant agents in meat and poultry products as well as fruits and vegetables: A review. *Critical Reviews in Food Science and Nutrition* 58 (3), 486–511 <https://doi.org/10.1080/10408398.2016.1194256>.
- Bastarrachea, L.J., Wong, D.E., Roman, M.J., Lin, Z., Goddard, J.M., 2015. Active packaging coatings. *Coatings* 5 (4), 771–791 <https://doi.org/10.3390/coatings5040771>.
- Biji, K.B., Ravishankar, C.N., Mohan, C.O., Gopal, T.K.S., 2015. Smart packaging systems for food applications: A review. *Journal of Food Science & Technology* 52 (10), 6125–6135 <https://doi.org/10.1007/s13197-015-1766-7>.
- Brockgreitens, J., Abbas, A., 2016. Responsive food packaging: Recent progress and technological prospects. *Comprehensive Reviews in Food Science and Food Safety* 15 (1), 3–15 <https://doi.org/10.1111/1541-4337.12174>.
- Byun, Y., Bae, H.J., Whiteside, S., 2012. Active warm-water fish gelatin film containing oxygen scavenging system. *Food Hydrocolloids* 27 (1), 250–255 <https://doi.org/10.1016/j.foodhyd.2011.06.010>.
- Chopra, S., Dhumal, S., Abeli, P., Beaudry, R., Almenar, E., 2017. Metal-organic frameworks have utility in adsorption and release of ethylene and 1-methylcyclopropene in fresh produce packaging. *Postharvest Biology and Technology* 130, 48–55 <https://doi.org/10.1016/j.postharvbio.2017.04.001>.
- Close, T., Tulsyan, G., Diaz, C.A., Weinstein, S.J., Richter, C., 2015. Reversible oxygen scavenging at room temperature using electrochemically reduced titanium oxide nanotubes. *Nature Nanotechnology* 10 (5), 418–422 <https://doi.org/10.1038/nnano.2015.51>.

- Coma, V., 2008. Bioactive packaging technologies for extended shelf life of meat-based products. *Meat Science* 78 (1–2), 90–103 <https://doi.org/10.1016/j.meatsci.2007.07.035>.
- Cooksey, K., 2010. Oxygen scavenging packaging systems. *Encyclopedia of polymer science and technology*. John Wiley & Sons, Inc <https://doi.org/10.1002/0471440264.pst570>.
- Correa, J.P., Molina, V., Sanchez, M., Kainz, C., Eisenberg, P., Massani, M.B., 2017. Improving ham shelf life with a polyhydroxybutyrate/polycaprolactone biodegradable film activated with nisin. *Food Packaging and Shelf Life* 11, 31–39 <https://doi.org/10.1016/j.foodpack.2016.11.004>.
- Cruz, R.S., Camilloto, G.P., Pires, A.C.S., 2012. Oxygen scavengers: An approach on food preservation. In: Eissa, A.A. (Ed.), *Structure and function of food engineering*. InTech, Rijeka, Croatia, pp. 21–42 <https://doi.org/10.5772/48453>.
- Dakal, T.C., Kumar, A., Majumdar, R.S., Yadav, V., 2016. Mechanistic basis of antimicrobial actions of silver nanoparticles. *Frontiers in Microbiology* 7, 1831 <https://doi.org/10.3389/fmicb.2016.01831>.
- Devlieghere, F., Debevere, J., 2000. Influence of dissolved carbon dioxide on the growth of spoilage bacteria. *LWT – Food Science and Technology* 33 (8), 531–537 <https://doi.org/10.1006/food.2000.0705>.
- Echeverría, I., López-Caballero, M.E., Gómez-Guillén, M.C., Mauri, A.N., Montero, M.P., 2018. Active nanocomposite films based on soy proteins-montmorillonite-clove essential oil for the preservation of refrigerated bluefin tuna (*Thunnus thynnus*) filets. *International Journal of Food Microbiology* 266, 142–149 <https://doi.org/10.1016/j.ijfoodmicro.2017.10.003>.
- Ejaz, M., Arfat, Y.A., Mulla, M., Ahmed, J., 2018. Zinc oxide nanorods/clove essential oil incorporated Type B gelatin composite films and its applicability for shrimp packaging. *Food Packaging and Shelf Life* 15, 113–121 <https://doi.org/10.1016/j.foodpack.2017.12.004>.
- Espitia, P.J.P., Soares, N.de F.F., Coimbra, J.S.R., de Andrade, N.J., Cruz, R.S., Medeiros, E.A.A., 2012. Bioactive peptides: Synthesis, properties, and applications in the packaging and preservation of food. *Comprehensive Reviews in Food Science and Food Safety* 11 (2), 187–204 <https://doi.org/10.1111/j.1541-4337.2011.00179.x>.
- Fang, Z., Zhao, Y., Warner, R.D., Johnson, S.K., 2017. Active and intelligent packaging in meat industry. *Trends in Food Science & Technology* 61 (2), 60–71 <https://doi.org/10.1016/j.tifs.2017.01.002>.
- Foltynowicz, Z., Bardenshtein, A., Sänglerlaub, S., Antvorskov, H., Kozak, W., 2017. Nanoscale, zero valent iron particles for application as oxygen scavenger in food packaging. *Food Packaging and Shelf Life* 11, 74–83 <https://doi.org/10.1016/j.foodpack.2017.01.003>.
- Gaikwad, K.K., Singh, S., Lee, Y.S., 2017a. A new pyrogallol coated oxygen scavenging film and their effect on oxidative stability of soybean oil under different storage conditions. *Food Science and Biotechnology* 26 (6), 1535–1543 <https://doi.org/10.1007/s10068-017-0232-x>.
- Gaikwad, K.K., Singh, S., Lee, Y.S., 2017b. A pyrogallol-coated modified LDPE film as an oxygen scavenging film for active packaging materials. *Progress in Organic Coatings* 111 (May), 186–195 <https://doi.org/10.1016/j.porgcoat.2017.05.016>.
- Ganiari, S., Choulitoudi, E., Oreopoulou, V., 2017. Edible and active films and coatings as carriers of natural antioxidants for lipid food. *Trends in Food Science & Technology* 68, 70–82 <https://doi.org/10.1016/j.tifs.2017.08.009>.
- Ghaani, M., Cozzolino, C.A., Castelli, G., Farris, S., 2016. An overview of the intelligent packaging technologies in the food sector. *Trends in Food Science & Technology* 51, 1–11 <https://doi.org/10.1016/j.tifs.2016.02.008>.
- Gharsallaoui, A., Joly, C., Oulahal, N., Degraeve, P., 2016. Nisin as a food preservative: Part 2: Antimicrobial polymer materials containing nisin. *Critical Reviews in Food Science and Nutrition* 56 (8), 1275–1289 <https://doi.org/10.1080/10408398.2013.763766>.
- Gómez-Estaca, J., López-de-Dicastillo, C., Hernández-Munoz, P., Catalá, R., Gavara, R., 2014. Advances in antioxidant active food packaging. *Trends in Food Science & Technology* 35 (1), 42–51 <https://doi.org/10.1016/j.tifs.2013.10.008>.
- Hafsa, J., Smach, M. ali, Ben Khedher, M.R., Charfeddine, B., Limem, K., Majdoub, H., et al., 2016. Physical, antioxidant and antimicrobial properties of chitosan films containing Eucalyptus globulus essential oil. *Lebensmittel-Wissenschaft und -Technologie*. Food Science and Technology 68, 356–364 <https://doi.org/10.1016/j.lwt.2015.12.050>.
- Haghighi-Manesh, S., Azizi, M.H., 2017. Active packaging systems with emphasis on its applications in dairy products. *Journal of Food Process Engineering* 40, e12542 <https://doi.org/10.1111/jfpe.12542>.
- Hansen, H., Hoy, M., Pettersen, M.K., 2009. Prediction of optimal CO<sub>2</sub> emitter capacity developed for modified atmosphere packaging of fresh salmon filets (*Salmo salar* L.). *Packaging Technology and Science* 22 (4), 199–208 <https://doi.org/10.1002/pts.843>.
- Hansen, H., Moen, B., Rodbotten, M., Berget, I., Pettersen, M.K., 2016. Effect of vacuum or modified atmosphere packaging (MAP) in combination with a CO<sub>2</sub> emitter on quality parameters of cod loins (*Gadus morhua*). *Food Packaging and Shelf Life* 9, 29–37 <https://doi.org/10.1016/j.foodpack.2016.05.005>.
- Holck, A.L., Pettersen, M.K., Moen, M.H., Sorheim, O., 2014. Prolonged shelf life and reduced drip loss of chicken filets by the use of carbon dioxide emitters and modified atmosphere packaging. *Journal of Food Protection* 77 (7), 1133–1141 <https://doi.org/10.4315/0362-028X.JFP-13-428>.
- Hoseinejad, M., Jafari, S.M., Katouzian, I., 2017. Inorganic and metal nanoparticles and their antimicrobial activity in food packaging applications. *Critical Reviews in Microbiology* 1–21, <https://doi.org/10.1080/1040841X.2017.1332001>.
- Huang, W.-H., Hsu, C.-K., Chiang, B.-H., 1999. Formulations of controlled atmosphere agents for packaged foods. *Journal of Agricultural and Food Chemistry* 47 (3), 906–910 <https://doi.org/10.1021/JF980770I>.
- Hurme, E., Thea, S.-M., Nielsen, R.A.T., 2002. Active and intelligent packaging. In: Ohlsson, T., Bengtsson, N. (Eds.), *Minimal processing technologies in the food industry*. Woodhead Publishing Limited, Cambridge, pp. 87–123 <https://doi.org/10.1533/9781855736795.87>.
- Hutter, S., Rügge, N., Yildirim, S., 2016. Use of palladium based oxygen scavenger to prevent discoloration of ham. *Food Packaging and Shelf Life* 8, 56–62 <https://doi.org/10.1016/j.foodpack.2016.02.004>.
- Islam, R.U., Khan, M.A., Islam, S.U., 2017. Plant derivatives as promising materials for processing and packaging of meat-based products - focus on antioxidant and antimicrobial effects. *Journal of Food Processing and Preservation* 41 (2), e12862 <https://doi.org/10.1111/jfpp.12862>.
- Iturriaga, L., Olabarrieta, I., Castellan, A., Gardrat, C., Coma, V., 2014. Active naringin-chitosan films: Impact of UV irradiation. *Carbohydrate Polymers* 110, 374–381 <https://doi.org/10.1016/j.carbpol.2014.03.062>.
- Jamshidian, M., Tehrani, E.A., Desobry, S., 2013. Antioxidants release from solvent-cast pla film: Investigation of pla antioxidant-active packaging. *Food and Bioprocess Technology* 6 (6), 1450–1463 <https://doi.org/10.1007/s11947-012-0830-9>.
- Johansson, K., Gillgren, T., Wineström, S., Järnström, L., Jönsson, L.J., 2014. Comparison of lignin derivatives as substrates for laccase-catalyzed scavenging of oxygen in coatings and films. *Journal of Biological Engineering* 8 (1), 1–10 <https://doi.org/10.1186/1754-1611-8-1>.
- Johnson, D.R., Tian, F., Roman, M.J., Decker, E.A., Goddard, J.M., 2015. Development of iron-chelating poly(ethylene terephthalate) packaging for inhibiting lipid oxidation in oil-in-water emulsions. *Journal of Agricultural and Food Chemistry* 63 (20), 5055–5060 <https://doi.org/10.1021/acs.jafc.5b00796>.
- Kaewklin, P., Siripatrawan, U., Suwanagul, A., Lee, Y.S., 2018. Active packaging from chitosan-titanium dioxide nanocomposite film for prolonging storage life of tomato fruit. *International Journal of Biological Macromolecules* 112, 523–529 <https://doi.org/10.1016/j.ijbiomac.2018.01.124>.
- Kanatt, S.R., Rao, M.S., Chawla, S.P., Sharma, A., 2012. Active chitosan-polyvinyl alcohol films with natural extracts. *Food Hydrocolloids* 29 (2), 290–297 <https://doi.org/10.1016/j.foodhyd.2012.03.005>.
- Kapetanakou, A.E., Skandamis, P.N., 2016. Applications of active packaging for increasing microbial stability in foods: Natural volatile antimicrobial compounds. *Current Opinion in Food Science* 12, 1–12 <https://doi.org/10.1016/j.cofs.2016.06.001>.
- Kerry, J.P., 2014. New packaging technologies, materials and formats for fast-moving consumer products. In: Han, J.H. (Ed.), *Innovations in food packaging*. Elsevier, San Diego, pp. 549–584 <https://doi.org/10.1016/B978-0-12-394601-0.00023-0>.
- Kösteki, M., Özdikicierlev, O., Cortés, C., Zulueta, A., Esteve, M.J., Frígola, A., 2016. Role of potassium permanganate ethylene on physicochemical properties, during storage of five different tomato cultivars. *MOJ Food Processing & Technology* 3 (2), 69 <https://doi.org/10.15406/mofjpt.2016.03.00069>.
- Kuswandi, B., 2017. Environmentally friendly food nano-packaging. *Environmental Chemistry Letters* 15 (2), 205–221 <https://doi.org/10.1007/s10311-017-0613-7>.
- Larson, A.M., Klibanov, A.M., 2013. Biocidal packaging for pharmaceuticals, foods, and other perishables. *Annual Review of Chemical and Biomolecular Engineering* 4 (1), 171–186 <https://doi.org/10.1146/annurev-chembioeng-061312-103253>.
- Lee, J.-S., Chang, Y., Lee, E.-S., Song, H.-G., Chang, P.-S., Han, J., 2018. Ascorbic acid-based oxygen scavenger in active food packaging system for raw meatloaf. *Journal of Food Science* 83 (3), 682–688 <https://doi.org/10.1111/1750-3841.14061>.
- Li, W., Li, L., Cao, Y., Lan, T., Chen, H., Qin, Y., 2017. Effects of PLA film incorporated with ZnO nanoparticle on the quality attributes of fresh-cut apple. *Nanomaterials* 7 (8), 207 <https://doi.org/10.3390/nano7080207>.
- Lin, Z., Decker, E.A., Goddard, J.M., 2016. Preparation of metal chelating active packaging materials by laminated photografting. *Journal of Coatings Technology and Research* 13 (2), 395–404 <https://doi.org/10.1007/s11998-015-9767-z>.
- Lin, Z., Goddard, J., 2018. Photo-curable metal-chelating coatings offer a scalable approach to production of antioxidant active packaging. *Journal of Food Science* 83 (2), 367–376 <https://doi.org/10.1111/1750-3841.14051>.
- Lin, Z., Roman, M.J., Decker, E.A., Goddard, J.M., 2016. Synthesis of iminodiacetate functionalized polypropylene films and their efficacy as antioxidant active-packaging materials. *Journal of Agricultural and Food Chemistry* 64 (22), 4606–4617 <https://doi.org/10.1021/acs.jafc.6b01128>.
- Maisanaba, S., Llana-Ruiz-Cabello, M., Gutiérrez-Praena, D., Pichardo, S., Puerto, M., Prieto, A.I., et al., 2017. New advances in active packaging incorporated with essential oils or their main components for food preservation. *Food Reviews International* 33 (5), 447–515 <https://doi.org/10.1080/87559129.2016.1175010>.
- Majid, I., Nayik, G.A., Dar, S.M., Nanda, V., 2017. Novel food packaging technologies: Innovations and future prospective. *Journal of the Saudi Society of Agricultural Sciences* <https://doi.org/10.1016/j.jssas.2016.11.003> <https://doi.org/10.1016/j.jssas.2016.11.003>.
- Mansourbahrani, S., Ghareyazie, B., Zarinnia, V., Kalatejari, S., Mohammadi, R.S., 2018. Study on the efficiency of ethylene scavengers on the maintenance of postharvest quality of tomato fruit. *Journal of Food Measurement and Characterization* <https://doi.org/10.1007/s11694-017-9682-3>.
- Martins, J.T., Cerqueira, M.A., Vicente, A.A., 2012. Influence of  $\alpha$ -tocopherol on physicochemical properties of chitosan-based films. *Food Hydrocolloids* 27 (1), 220–227 <https://doi.org/10.1016/j.foodhyd.2011.06.011>.
- Mellinas, C., Valdés, A., Ramos, M., Burgos, N., Garrigós, M., del, C., et al., 2016. Active edible films: Current state and future trends. *Journal of Applied Polymer Science* 133 (2), 42631 <https://doi.org/10.1002/app.42971>.
- Nieva-Echevarría, B., Manzano, M.J., Goicoechea, E., Guillén, M.D., 2015. 2,6-Di-Tert-Butyl-Hydroxytoluene and its metabolites in foods. *Comprehensive Reviews in Food Science and Food Safety* 14 (1), 67–80 <https://doi.org/10.1111/1541-4337.12121>.
- Nisa, I. u, Ashwar, B.A., Shah, A., Gani, A., Gani, A., Masoodi, F.A., 2015. Development of potato starch based active packaging films loaded with antioxidants and its effect

- on shelf life of beef. *Journal of Food Science & Technology* 52 (11), 7245–7253 <https://doi.org/10.1007/s13197-015-1859-3>.
- Otoni, C.G., Espitia, P.J.P., Avena-Bustillos, R.J., McHugh, T.H., 2016. Trends in antimicrobial food packaging systems: Emitting sachets and absorbent pads. *Food Research International* 83, 60–73 <https://doi.org/10.1016/j.foodres.2016.02.018>.
- Padrão, J., Gonçalves, S., Silva, J.P., Sencadas, V., Lanceros-Méndez, S., Pinheiro, A.C., et al., 2016. Bacterial cellulose-lactoferrin as an antimicrobial edible packaging. *Food Hydrocolloids* 58, 126–140 <https://doi.org/10.1016/j.foodhyd.2016.02.019>.
- Pagno, C.H., de Farias, Y.B., Costa, T.M.H., Rios, A. de O., Flôres, S.H., 2016. Synthesis of biodegradable films with antioxidant properties based on cassava starch containing bixin nanocapsules. *Journal of Food Science & Technology* 53 (8), 3197–3205 <https://doi.org/10.1007/s13197-016-2294-9>.
- Pant, A.F., Sangerlaub, S., Muller, K., 2017. Gallic acid as an oxygen scavenger in bio-based multilayer packaging films. *Materials* 10, 489 <https://doi.org/10.3390/ma10050489>.
- Petersen, M.K., Hansen, M., Mielnik, M., 2014. Effect of different packaging methods on quality and shelf life of fresh reindeer meat. *Packaging Technology and Science* 27 (12), 987–997 <https://doi.org/10.1002/pts.2075>.
- Piñeros-Hernandez, D., Medina-Jaramillo, C., López-Córdoba, A., Goyanes, S., 2017. Edible cassava starch films carrying rosemary antioxidant extracts for potential use as active food packaging. *Food Hydrocolloids* 63, 488–495 <https://doi.org/10.1016/j.foodhyd.2016.09.034>.
- Pokorný, J., 2007. Are natural antioxidants better - and safer - than synthetic antioxidants? *European Journal of Lipid Science and Technology* 109 (6), 629–642 <https://doi.org/10.1002/ejlt.200700064>.
- Poyatos-Racionero, E., Ros-Lis, J.V., Vivanco, J.L., Martínez-Máñez, R., 2018. Recent advances on intelligent packaging as tools to reduce food waste. *Journal of Cleaner Production* 172, 3398–3409 <https://doi.org/10.1016/j.jclepro.2017.11.075>.
- Realini, C.E., Marcos, B., 2014. Active and intelligent packaging systems for a modern society. *Meat Science* 98 (3), 404–419 <https://doi.org/10.1016/j.meatsci.2014.06.031>.
- Remya, S., Mohan, C.O., Venkateshwarlu, G., Sivaraman, G.K., Ravishankar, C.N., 2017. Combined effect of O<sub>2</sub> scavenger and antimicrobial film on shelf life of fresh cobia (*Rachycentron canadum*) fish steaks stored at 2 °C. *Food Control* 71, 71–78 <https://doi.org/10.1016/j.foodcont.2016.05.038>.
- Restuccia, D., Spizzirri, U.G., Parisi, O.L., Cirillo, G., Curcio, M., Iemma, F., et al., 2010. New EU regulation aspects and global market of active and intelligent packaging for food industry applications. *Food Control* 21 (11), 1425–1435 <https://doi.org/10.1016/j.foodcont.2010.04.028>.
- Rhim, J.-W., Park, H.-M., Ha, C.-S., 2013. Bio-nanocomposites for food packaging applications. *Progress in Polymer Science* 38 (10–11), 1629–1652 <https://doi.org/10.1016/j.progpolymsci.2013.05.008>.
- Ribeiro-Santos, R., Andrade, M., Melo, N. R. de, Sanches-Silva, A., 2017. Use of essential oils in active food packaging: Recent advances and future trends. *Trends in Food Science & Technology* 61, 132–140 <https://doi.org/10.1016/j.tifs.2016.11.021>.
- Röcker, B., Rüegg, N., Glöss, A.N., Yeretizian, C., Yildirim, S., 2017. Inactivation of palladium-based oxygen scavenger system by volatile sulfur compounds present in the headspace of packaged food. *Packaging Technology and Science* 30, 427–442 <https://doi.org/10.1002/pts.2220>.
- Rollini, M., Nielsen, T., Musatti, A., Limbo, S., Piergiovanni, L., Hernandez Munoz, P., et al., 2016. Antimicrobial performance of two different packaging materials on the microbiological quality of fresh salmon. *Coatings* 6 (1), 6 <https://doi.org/10.3390/coatings6010006>.
- Roman, M.J., Decker, E.A., Goddard, J.M., 2015. Performance of nonmigratory iron chelating active packaging materials in viscous model food systems. *Journal of Food Science* 80 (9), E1965–E1973 <https://doi.org/10.1111/1750-3841.12972>.
- Roman, M.J., Decker, E.A., Goddard, J.M., 2016. Retaining oxidative stability of emulsified foods by novel nonmigratory polyphenol coated active packaging. *Journal of Agricultural and Food Chemistry* 64 (27), 5574–5582 <https://doi.org/10.1021/acs.jafc.6b01933>.
- Sanches-Silva, A., Costa, D., Albuquerque, T.G., Buonocore, G.G., Ramos, F., Castilho, M.C., et al., 2014. Trends in the use of natural antioxidants in active food packaging: A review. *Food Additives & Contaminants: Part A* 31 (3), 374–395 <https://doi.org/10.1080/19440049.2013.879215>.
- Scarfato, P., Avallone, E., Galdi, M.R., Di Maio, L., Incarnato, L., 2017. Preparation, characterization, and oxygen scavenging capacity of biodegradable  $\alpha$ -tocopherol/PLA micro-particles for active food packaging applications. *Polymer Composites* 38, 981–986 <https://doi.org/10.1002/pc.23661>.
- Schumann, B., Schmid, M., 2018. Packaging concepts for fresh and processed meat – recent progresses. *Innovative Food Science & Emerging Technologies* 47, 88–100 <https://doi.org/10.1016/j.ifset.2018.02.005>.
- Severino, R., Ferrari, G., Vu, K.D., Donsì, F., Salmieri, S., Lacroix, M., 2015. Antimicrobial effects of modified chitosan based coating containing nanoemulsion of essential oils, modified atmosphere packaging and gamma irradiation against *Escherichia coli* O157:H7 and *Salmonella* Typhimurium on green beans. *Food Control* 50, 215–222 <https://doi.org/10.1016/j.foodcont.2014.08.029>.
- Silva-Weiss, A., Ihl, M., Sobral, P.J.A., Gómez-Guillén, M.C., Bifani, V., 2013. Natural additives in bioactive edible films and coatings: Functionality and applications in foods. *Food Engineering Reviews* 5 (4), 200–216 <https://doi.org/10.1007/s12393-013-9072-5>.
- Silva, M.F., Lopes, P.S., Da Silva, C.F., Yoshida, C.M.P., 2016. Active packaging material based on buriti oil - mauritia flexuosa L.f. (Arecaceae) incorporated into chitosan films. *Journal of Applied Polymer Science* 133 (12), 43210 <https://doi.org/10.1002/app.43210>.
- Silva, N.H.C.S., Vilela, C., Almeida, A., Marrucho, I.M., Freire, C.S.R., 2018. Pullulan-based nanocomposite films for functional food packaging: Exploiting lysozyme nanofibers as antibacterial and antioxidant reinforcing additives. *Food Hydrocolloids* 77, 921–930 <https://doi.org/10.1016/j.foodhyd.2017.11.039>.
- Sivertsvik, M., Jeksrud, W.K., Rosnes, J.T., 2002. A review of modified atmosphere packaging of fish and fishery products - significance of microbial growth, activities and safety. *International Journal of Food Science and Technology* 37 (2), 107–127 <https://doi.org/10.1046/j.1365-2621.2002.00548.x>.
- Souza, M.P., Vaz, A.F.M., Silva, H.D., Cerqueira, M.A., Vicente, A.A., Carneiro-da-Cunha, M.G., 2015. Development and characterization of an active chitosan-based film containing quercetin. *Food and Bioprocess Technology* 8 (11), 2183–2191 <https://doi.org/10.1007/s11947-015-1580-2>.
- Spricigo, P.C., Foschini, M.M., Ribeiro, C., Corrêa, D.S., Ferreira, M.D., 2017. Nanoscaled platforms based on SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> impregnated with potassium permanganate use color changes to indicate ethylene removal. *Food and Bioprocess Technology* 10 (9), 1622–1630 <https://doi.org/10.1007/s11947-017-1929-9>.
- Tas, C.E., Hendessi, S., Baysal, M., Unal, S., Cebeci, F.C., Menciloglu, Y.Z., et al., 2017. Halloysite nanotubes/polyethylene nanocomposites for active food packaging materials with ethylene scavenging and gas barrier properties. *Food and Bioprocess Technology* 10 (4), 789–798 <https://doi.org/10.1007/s11947-017-1860-0>.
- Tian, F., Decker, E.A., Goddard, J.M., 2012. Control of lipid oxidation by nonmigratory active packaging films prepared by photoinitiated graft polymerization. *Journal of Agricultural and Food Chemistry* 60 (31), 7710–7718 <https://doi.org/10.1021/jf302377b>.
- Tian, F., Decker, E.A., Goddard, J.M., 2013a. Controlling lipid oxidation of food by active packaging technologies. *Food & Function* 4, 669–680 <https://doi.org/10.1039/c3fo30360h>.
- Tian, F., Decker, E.A., Goddard, J.M., 2013b. Controlling lipid oxidation via a biomimetic iron chelating active packaging material. *Journal of Agricultural and Food Chemistry* 61 (50), 12397–12404 <https://doi.org/10.1021/jf4041832>.
- Tian, F., Decker, E.A., McClements, D.J., Goddard, J.M., 2014. Influence of non-migratory metal-chelating active packaging film on food quality: Impact on physical and chemical stability of emulsions. *Food Chemistry* 151, 257–265 <https://doi.org/10.1016/j.foodchem.2013.11.074>.
- Tulsyan, G., Richter, C., Diaz, C.A., 2017. Oxygen scavengers based on titanium oxide nanotubes for packaging applications. *Packaging Technology and Science* 30, 251–256 <https://doi.org/10.1002/pts.2296>.
- Valdés, A., Mellinas, A.C., Ramos, M., Burgos, N., Jiménez, A., Garrigós, M.C., 2015. Use of herbs, spices and their bioactive compounds in active food packaging. *RSC Advances* 5, 40324–40335 <https://doi.org/10.1039/C4RA17286H>.
- Valdés, A., Mellinas, A.C., Ramos, M., Garrigós, M.C., Jiménez, A., 2014. Natural additives and agricultural wastes in biopolymer formulations for food packaging. *Frontiers in Chemistry* 2, 6 <https://doi.org/10.3389/fchem.2014.00006>.
- Vilela, C., Pinto, R.J.B., Coelho, J., Domingues, M.R.M., Daina, S., Sadocco, P., et al., 2017. Bioactive chitosan/ellagic acid films with UV-light protection for active food packaging. *Food Hydrocolloids* 73, 120–128 <https://doi.org/10.1016/j.foodhyd.2017.06.037>.
- Wang, H., Qian, J., Ding, F., 2018. Emerging chitosan-based films for food packaging applications. *Journal of Agricultural and Food Chemistry* 66 (2), 395–413 <https://doi.org/10.1021/acs.jafc.7b04528>.
- Wang, Y., Xia, Y., Zhang, P., Ye, L., Wu, L., He, S., 2017. Physical characterization and pork packaging application of chitosan films incorporated with combined essential oils of cinnamon and ginger. *Food and Bioprocess Technology* 10 (3), 503–511 <https://doi.org/10.1007/s11947-016-1833-8>.
- Werner, B.G., Koontz, J.L., Goddard, J.M., 2017. Hurdles to commercial translation of next generation active food packaging technologies. *Current Opinion in Food Science* 16, 40–48 <https://doi.org/10.1016/j.cofs.2017.07.007>.
- Wong, D.E., Andler, S.M., Lincoln, C., Goddard, J.M., Talbert, J.N., 2017. Oxygen scavenging polymer coating prepared by hydrophobic modification of glucose oxidase. *Journal of Coatings Technology and Research* 14 (2), 489–495 <https://doi.org/10.1007/s11998-016-9865-6>.
- Wrona, M., Cran, M.J., Nérin, C., Bigger, S.W., 2017. Development and characterisation of HPMC films containing PLA nanoparticles loaded with green tea extract for food packaging applications. *Carbohydrate Polymers* 156, 108–117 <https://doi.org/10.1016/j.carbpol.2016.08.094>.
- Wyrwa, J., Barska, A., 2017. Innovations in the food packaging market: Active packaging. *European Food Research and Technology* 243, 1681–1692 <https://doi.org/10.1007/s00217-017-2878-2>.
- Xia, Y., Rubino, M., 2016. Effect of cut edge area on the migration of BHT from polypropylene film into a food simulant. *Polymer Testing* 51, 190–194 <https://doi.org/10.1016/j.polytest.2016.03.016>.
- Yang, W., Owczarek, J.S., Fortunati, E., Kozanecki, M., Mazzaglia, A., Balestra, G.M., et al., 2016. Antioxidant and antibacterial lignin nanoparticles in polyvinyl alcohol/chitosan films for active packaging. *Industrial Crops and Products* 94, 800–811 <https://doi.org/10.1016/j.indcrop.2016.09.061>.
- Yildirim, S., Röcker, B., Petersen, M.K., Nilsen-Nygaard, J., Ayhan, Z., Rutkaite, R., et al., 2018. Active packaging applications for food. *Comprehensive Reviews in Food Science and Food Safety* 17, 165–199 <https://doi.org/10.1111/1541-4337.12322>.
- Yildirim, S., Röcker, B., Rüegg, N., Lohwasser, W., 2015. Development of palladium-based oxygen scavenger: Optimization of substrate and palladium layer thickness. *Packaging Technology and Science* 28 (8), 710–718 <https://doi.org/10.1002/pts.2134>.
- Yuan, G., Chen, X., Li, D., 2016. Chitosan films and coatings containing essential oils: The antioxidant and antimicrobial activity, and application in food systems. *Food Research International* 89, 117–128 <https://doi.org/10.1016/j.foodres.2016.10.004>.
- Zhang, J., Cheng, D., Wang, B., Khan, I., Ni, Y., 2017. Ethylene control technologies in extending postharvest shelf life of climacteric fruit. *Journal of Agricultural and Food Chemistry* 65 (34), 7308–7319 <https://doi.org/10.1021/acs.jafc.7b02616>.