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Smart Polymers for Food and Water Quality Control and Safety

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Abstract

A large number of annual cases of diseases and deaths related to spoiled or contaminated food, and the amount of food waste are a matter of socio-economic impact, highlighting the need for a fast, easy, cheap, available, and real-time determination of food quality and safety. To ensure this, physical and chemical food quality indicators such as humidity, temperature, gases, pH, microorganisms, pesticides, etc., should be controlled and monitored during production, transportation, storage, and consumption. In this sense, smart polymers are raised as useful tools to facilitate this task. These polymers are sensitive to variations in the microenvironment, modifying their properties and/or generating a response that can be measured. Due to their versatility, these materials can be part of the food packaging to inform the consumers or be used as a measuring tool to determine the state of the food. This chapter envisaged the concept of smart polymers, the types, and their main applications for determining food quality and ensuring food and beverage safety.

Keywords: smart polymer, food control and safety, food quality indicators, polymer sensor, stimuli-responsive polymer

1. INTRODUCTION

The World Health Organization reported that 10% of the population falls ill after eating contaminated food every year, causing over 420,000 deaths and 550 million cases of diarrheal disease, among other 200 different diseases. Spoiled food can occur at any point of the manufacturing chain, and is undesirable for consumption, changes the food's texture, appearance, odor and flavor. It is estimated that around 30% of food is wasted [1] from production to consumption due to poor food management and contamination [2], with a concomitant socio-economic impact.

Food safety refers to the procedures, regarding the handling, preparation, and storage of the different foods, to prevent foodborne illnesses. In this sense food quality implies numerous factors, including nutritional values, stability, consumer standards, and food health. Even though factors vary according to the different countries [3], the expiration date is taken as a reference to estimate foods and beverages' end-life. However, this reference does not account for the actual food state and whether it is safe or not to eat, since no information about the handling, manufacture, and transportation conditions are available. For this reason, raising real-time food quality control systems is a need to ensure consumer's health and avoid unnecessary food waste.

Several physical and chemical quality indicators can be measured both qualitatively and quantitatively to ensure food and beverage safety, such as different gases, humidity, temperature, pH, microorganisms, pesticides, biotoxins, persistent organic pollutants, etc. Early detection of these real food's state indicators would reduce the number of foodborne diseases in consumers [4]. However, traditional measuring techniques are expensive, time-consuming, they are not available for consumers, and, above all, they do not allow real-time and *in-situ* determination. As a result, researchers have directed their interest to develop and apply different food quality indicator measuring techniques to ensure food and water quality, including smart polymers.

Polymer science and technology is currently oriented to the development of polymers with special functionalities to be used in many fields such as aeronautics, packaging, electronics, construction, medical, etc. Polymers are tuneable materials with a wide range of physical and chemical properties derived from their structure. As defined by García et al. [5] a smart polymer generates a response to a stimulus through a specific mechanism. For example, they can be sensitive to their microenvironment modifying their properties and produce a measurable response to specific targets. Smart polymers in the food industry are a user-friendly tool that allows obtaining real-time information about food state and safety, can either be part of the packaging, or be used to measure food quality parameters in the food.

This book chapter shows the potential of smart polymers according to their application in food quality and safety control. The chapter comprises two main sections, the first of which describes the concept of smart polymers, while the second describes the uses of smart polymers for quality control and food safety based on quality indicators.

2. SMART POLYMERS

As mentioned in the introduction, a smart polymer responds to a stimulus through a specific mechanism. Consequently, they can be classified according to the response, the stimulus, or the mechanism by which the response is produced, as depicted in **Figure 1**. Among the different classifications, we can classify them as i) stimuli-responsive polymers, and ii) sensory polymers. The former response to the stimulus with an action, such as a variation in the volume or shape, in the interaction with solvents, generation/break of chemical bonds, etc. The latter responds with an alert, that is, useful analytical information. However, both types of smart polymers can respond to any type of stimulus, through any mechanism, and even show visual macroscopic signals (see examples in **Figure 1**).

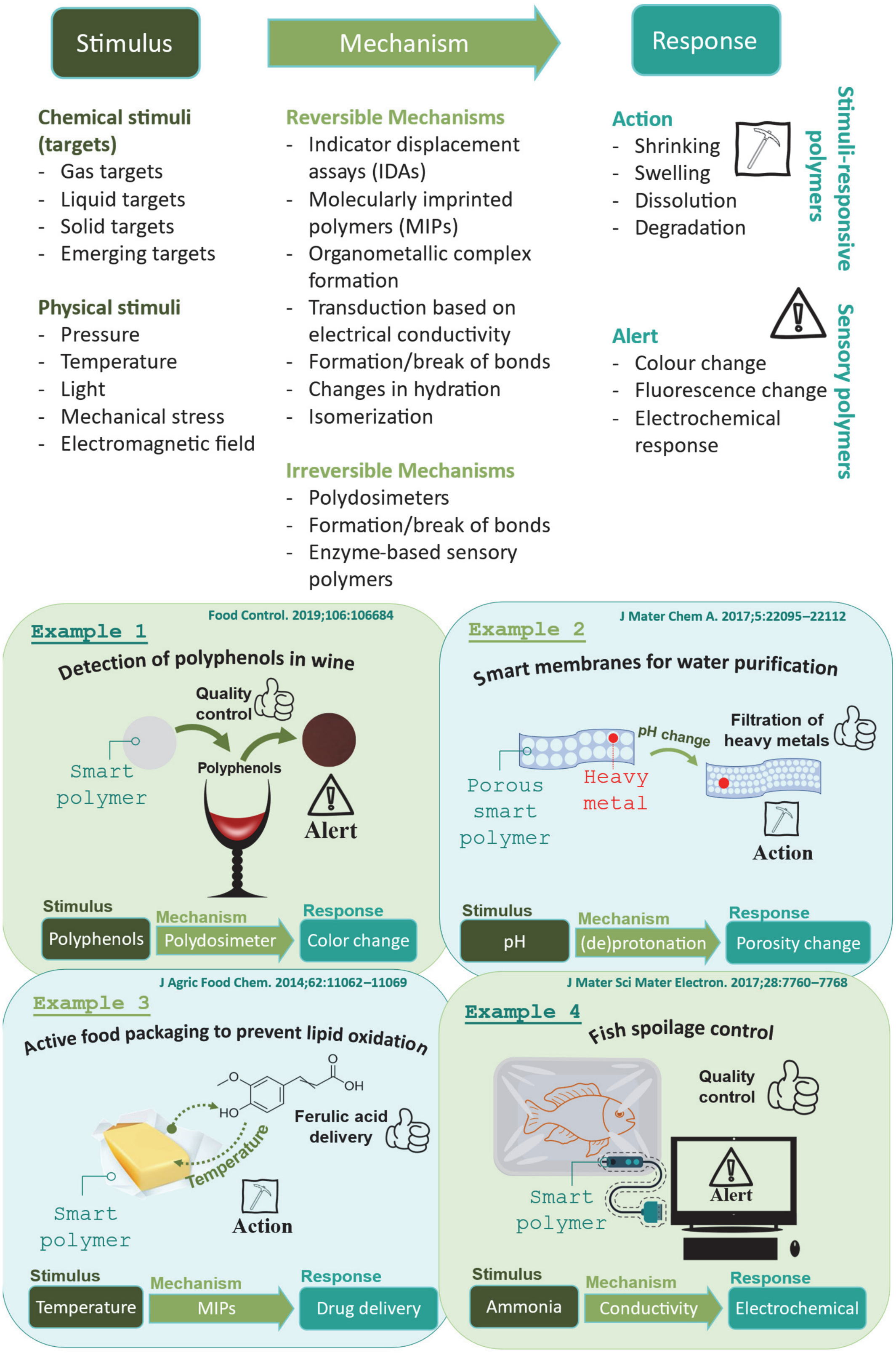

Figure 1. Classification of smart polymers according to the stimulus, the responsive mechanism, or the produced response.

Alt-Text: Classification of the of smart polymers according to the type of stimulus (chemical of physical), the responsive mechanism (reversible or irreversible) and the response they produce (action-stimuli responsive polymer, or alert-sensory polymer). Also, four examples of different smart polymers in which the stimulus, the mechanism and the responsonse are specified.

Long description: Classification of the of smart polymers according to the type of stimulus (chemical of physical), the responsive mechanism (reversible or irreversible) and the response they produce (action-stimuli responsive polymer, or alert-sensory polymer). Also, four examples of different smart polymers are given. The first one is the detection of polyphenols in wine using a polydosimeter and producing a color change. The second one is a smart membrane for water purification in which a pH variation deprotonates the membrane causing a porosity change. The third one is an active food packaging containing a MIP in which a variation of the temperature produces a drug release. The last one is a smart polymer that changes the conductivity in the presence of ammonia, producing a measurable electrochemical response.

2.1. Stimuli-responsive polymers

Stimuli-responsive polymers show a drastic change in a physical property caused by an answer to a small environmental factor variation, such as temperature, pH, light, the presence of target molecules (chemical or biochemical), electromagnetic field, etc.; and they are related to solvent-polymer interactions, physical state, hydrophilic/lipophilic rates, or solubility, among others. As a result, they cause different answers in the polymer, such as formation/break of secondary interactions, simple reactions (oxidation, reduction, acid-base, hydrolysis, etc.), changes in the solubility or the size, or conformational variations in the structure, also leading to absorption or releasing processes. Stimuli-responsive polymers are unique materials since they can be tailored by selecting the polymer backbone and the functional groups to control the different processes. For this reason, they are widely investigated for controlled drug delivery systems as well [6].

The number of stimuli-responsive polymers is vast, and only a few examples will be mentioned here. On the one hand, physical stimuli modify the polymer's chain dynamics, such as the polymer/solvent system. In this sense, the most widely studied are temperature-responsive polymers, like lower critical solution temperature (LCST) polymers. Poly(*N*-isopropylacrylamide) (PNIPAM) is the most representative example, which varies from transparent to opaque or vice versa at about 32 ˚C due to a phase transition resulting from intra- or inter-chain weakening/strengthening of hydrogen bonds. Another common physical stimulus is pH. The pH responsive polymers have ionizable functional groups that protonates/deprotonates upon environmental pH variations, such as acrylic acid and *N,N*-dimethylaminoethyl methacrylate (DMAEMA). Moreover, light-responsive polymers show isomerization or bond-breaking upon light irradiation and common examples include azobenzene monomers-containing polymers. On the other hand, chemical stimuli vary molecular interactions between the polymer and the solvent or between polymer chains. The most studied are biological stimuli-responsive polymers that modify the functioning of molecules, i.e., the interaction with the biomolecules results in polymeric network crosslinking and/or ionization [6].

2.2. Sensory polymers

Sensors are based on two integrated subunits, one of them acts as the receptor subunit, able to interact with an analyte or a target molecule, and the other one is the indicator subunit, which delivers a readable signal. If the interaction is reversible, they are called chemical sensors or chemosensors, while they are called chemical dosimeters if the interaction is not reversible. However, we will use the term chemical sensors for both situations. The detection phenomena rely on the indicator subunit or transducer, that transforms the interaction into a measurable property (color, fluorescence, conductivity, etc.).

Most of the research related to chemical sensors is based on discrete molecules with low molecular weight, low chemical and thermal resistances, and which are difficult to recover. The immobilization of these chemical sensors in polymeric matrixes allows for obtaining solid sensory materials that do not migrate, with good mechanical properties, tunable in shape and properties. But, more importantly, polymer sensors are low-cost, simplified sensing counterparts of complex analytical techniques adapted for non-specialized users. In this sense, polymeric chemosensors can be designed to have functional monomers in their structure to detect discrete molecules (anions, cations, or neutral molecules), or they can even be further functionalized by covalently bonding larger biological macromolecules on the polymeric substrate, such as enzymes or antibodies.

A relevant group of polymer sensors is optical sensors, namely, optodes. These devices allow the identification of substances of interest by modifications of the transducer's optical properties, once the reaction between the receptor and the analyte takes place. Among the most widely used optical detection techniques are colorimetry, absorbance, fluorescence, luminescence, chemiluminescence, energy transfer, or reflectance by measuring light intensity in different spectrum regions (from UV to IR) stand out. In some of these techniques, the determination can be done by the naked eye or with the help of simple and inexpensive equipment, which is very useful for non-specialized personnel, especially those of colorimetry or luminescence.

Another recognition and transduction mechanism worth mentioning here is related to conductive polymers due to their sensitivity. They show an electric response, a variation of their electrical properties, in the presence of a stimulus, which can be analyzed by amperometry, voltammetry, conductometry, etc. However, they are also used as electric field-responsive polymers. In addition, these polymers can also show a visual response through a color or fluorescence change. Common conductive polymers include polyaniline (PAni), poly(3,4-ethylenedioxythiophene) (PEDOT), or polypyrrole (PPy) [7]. Also, the electron-conducting ability of these polymers contributes either by enhancing or by quenching the luminescence as the transductor of the smart sensing devices in the presence of the desired molecules.

2.3. Special cases

Some polymers can be used both as sensory polymers and as stimuli-responsive polymers, in other words, they are a valid tool for any type of smart polymers. The most notable special cases are molecularly imprinted polymers (MIPs) and polymers with immobilized biomolecules.

2.3.1. Molecularly imprinted polymers

MIPs are examples of synthetic materials used for molecular recognition and raised to mimic biosensors. They are robust, cheaper than natural materials, and can be synthesized to recognize molecules that natural receptors cannot. In the presence of a template, functional monomers forming a complex through non-covalent interactions (hydrogen bonds, Van der Waals, or π-π interactions) are polymerized together with a crosslinker, forming a polymeric network. Then, the template is removed, leaving recognition sites within the polymer (**Figure 2**). The template should be similar to (or the same as) the target molecule in chemical functionality, shape and size to rebind with the target. MIPs serve as adsorption sites to coat the electrodes' surfaces and increase their selectivity in techniques such as potentiometry or voltammetry [8].

The most popular functional monomers used to prepare MIPs are methacrylic acid (MMA), 3-aminopropyl-triethoxysilane (APTES), and phenyltrimethoxysilane (PTES). These functional monomers are always co-polymerized with cross-linkers, such as ethylene glycol dimethacrylate (EGDMA) and tetraethyl orthosilicate (TEOS). Other interesting monomers for electropolymerization without crosslinker are o-phenylenediamine, pyrrole, dopamine, o-aminophenol and *p*-aminothiophenol.

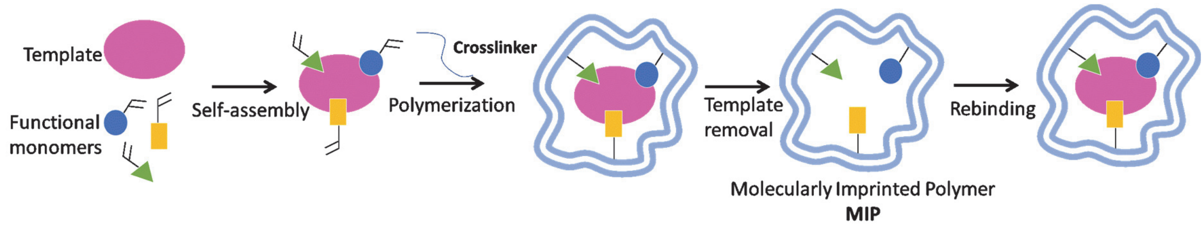

Figure 2. Schematic representation of the preparation of MIPs.

Alt-Text: Descripiton of MIPs preparation. The template and the functional monomers are self-assembled and then polymerized together with a crosslinker. After the template removal, the MIP is ready to serve as a smart polymer and rebind with a target molecule.

2.3.2. Polymers with immobilized biomolecules

The immobilization of biomolecules in polymeric materials has been used for decades. It is a resource used in different fields of science, although its benefits are known especially in medicine and food/beverage control. There are many types of polymers for the immobilization of biomolecules, and there are several ways to carry out this immobilization. García et al. [5] classified these polymers as type 1, type 2, pseudo-type 2 and type 3 smart polymers, based on their complexity level.

Typical immobilized biomolecules include antibodies (for the detection of antigens), proteases (enzymes for the proteolysis of substrates), DNA, RNA, etc. and are intended for the recognition or to produce a response in the presence of large biomolecules. The most remarkable advantage of this type of smart polymer is that they allow easy handling. Without the support offered by polymers, these biomolecules are generally more unstable, and their management involves more complex experimental procedures.

2.4. Application of smart polymers

These smart polymers have several applications, such as drug delivery systems, tissue engineering, cell culture supports, antifouling coatings, sensors, and actuators systems among others, and they can be prepared in the shape of films, fibers, coatings, micelles, etc. according to their final applications. Regarding their use in food quality control and safety, the most convenient shape they are applied as is films or coatings, to be integrated as part of the food packaging. Traditional food packaging is designed to be as inert as possible, to protect, communicate, and be convenient. The packaging is a shield against external environmental conditions such as heat, light, moisture, gas emission, pathogens, etc. The information printed on the surface communicates valuable information about the food inside, and they are also meant to save time for consumers and to facilitate different sizes and shapes [10]. On the contrary, active or smart food packagings are far more than an informative barrier against pernicious external factors. They are designed to provide additional protection to the consumer by revealing the foodstuff's state before being directly exposed to it, after the interaction with a specific compound or change in the package environment. For example, triggered by an external stimulus, active packaging can change its conditions to extend the shelf life or to improve the quality and safety of the food inside by the controlled release of encapsulated components such as salt, CO_2, or by controlling the moisture, the temperature, or the gaseous concentration [11]. On the other hand, sensory polymers can selectively interact with a target molecule and transform that information into an optical or electrochemical response. When used in food packaging, sensory polymers become a simple, rapid, and cheap means to visually obtain information about the food state (**Figure 3**).

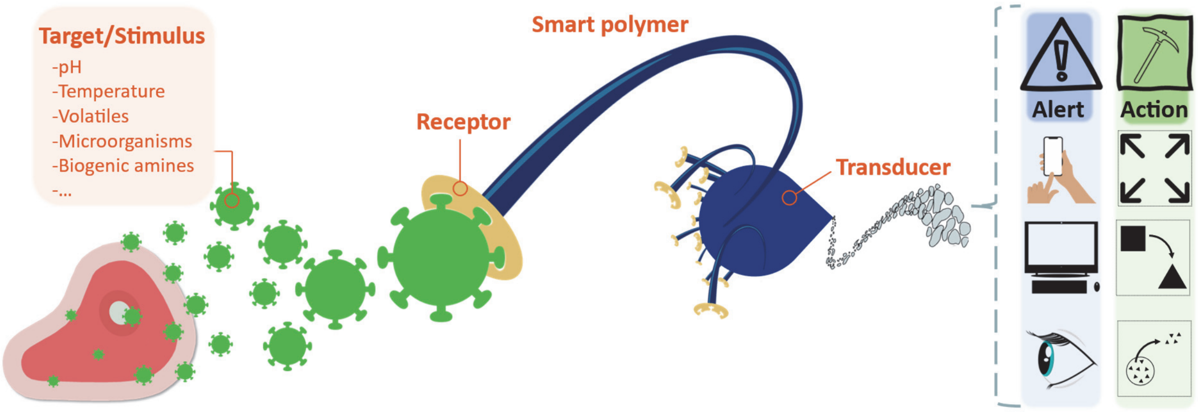

Figure 3. Detection of food quality indicators by a smart polymer and transduction.

Alt-text: Detection mechanism of food quality indicators. The target molecule or the stimulus is detected by the receptor of the smart polymer and then transduced into a measurable alert or action.

In general, targets for food quality control and safety can either be a physical (temperature, light, mechanical stress, etc) or a chemical stimulus (pH, chemical species, redox oxidation, etc.), or even a biomolecule (enzyme, pathogen). Although we won't tackle all of them, the main stimulus that are useful food quality indicators are envisaged in the next section.

3. FOOD QUALITY AND SAFETY TARGETS FOR SMART POLYMERS

As previously mentioned, contaminated food causes a great number of deaths and diseases every year, and specific indicators are needed to evaluate the state of the food product. This section discusses and explains the main indicators of the quality and safety of food and beverages (**Figure 4**). Although we made up a classification based on the type of indicator, it is important to highlight that most of the time all of them are closely related, since when a food product deteriorates, multiple markers alert simustaneously about the state of that product.

The main characteristics and the functioning of the developed smart polymers for the detection or elimination of these analytes are also included and some examples. In addition, commercialized smart polymers for food quality and safety are also included.

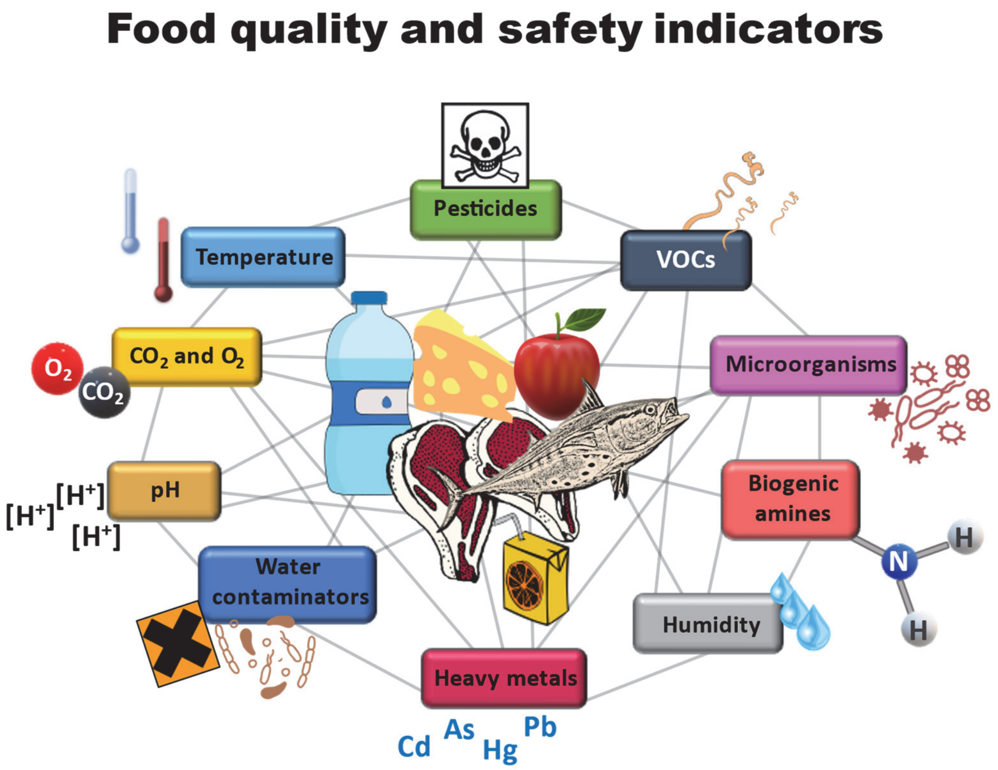

Figure 4: Main food and water quality and safety indicators, closely related and dependent. Alt-Text: Representation of the main targets of food and water quality and safety (temperature, gases, pH, heavy metals, humidity, volatile organic compounds (VOCs), pesticides, water contaminators, and biogenic amines) and how they are closely related and depend on each other.

3.1. Gas indicators

The main food quality gas targets are carbon dioxide (CO_2), oxygen (O_2), volatile organic compounds (VOCs), and BAs (BAs). These types of indicators are especially important in modified atmosphere packaged (MAP) food products, being CO_2 the most used gas in the food industry.

3.1.1. Carbon dioxide and oxygen

High CO_2 concentrations are used in MAP food since it inhibits bacterial and fungal growth and decreases the environmental pH. Its antimicrobial activity mechanism is based on avoiding decarboxylation due to the anaerobic atmosphere. Amino acid decarboxylation produces the release of BAs, which are another significant quality and safety food indicator later mentioned. In addition, CO_2 accumulation disturbs the membrane permeability of some microorganisms [4], and fresh food bacteria increase CO_2 in the environment owing to breathing processes. Therefore, CO_2 concentration reduction in fresh food indicates the drop-off of modified atmosphere packaging, and, on the other hand, the increase in the CO_2 levels causes food freshness to lessen [12].

Another key gas for food quality is O_2, which is crucial for the biological activity of several microorganisms. The increase of O_2 in MAP causes oxidative reactions in food, such as fat oxidation, browning reactions, and pigment oxidation [4] prompting flavor deterioration, odor changes, aerobic bacteria growth, and decreasing the nutritional food value. On the other hand, a decrease in O_2 can be associated with aerobic microorganisms' activity; therefore, alterations in the O_2 concentration in fresh food indicate a food quality loss, accelerating food spoilage [13].

3.1.2. Volatile organic compounds

VOCs include a wide range of natural and synthetic chemicals such as alcohols, hydrocarbons, carbonyls, sulfur, and nitrogen-containing compounds. The presence of VOCs in food arises from different sources: i) they are released by microbial activity in perishable food such as milk, meat, seafood, fruits, and vegetables; ii) they are used in product processing; and iii) they are derived from different steps in the food industry, fermentation, cooking, cleaning, disinfection, and others.

Ethanol, lactic acid, and acetic acid are the main secondary metabolites produced in fermentation. An increase in ethanol levels and simultaneous low O_2 and high CO_2 concentrations indicate anaerobic bacteria growth in fresh food. In addition, both acetate and acetic acid levels rise with the storage time in fresh fish and meat under MAP [12].

The major volatile basic nitrogen compounds produced by microbial activity activity mainly in fresh fish are trimethylamine, ammonia, and dimethylamine and their presence is directly related to the microbial deterioration of food [14]. On the other hand, volatile sulfur compounds are naturally generated in food and present a high impact on food aroma in many products such as bread, wine, vegetables, coffee, or chicken, and contribute to food flavor in chocolate, cheese, tropical fruits or cereals [15]. They are an important indicator of food fresh quality as well. In addition, volatile sulfur compounds are responsible for food off-flavor.

3.1.3. Biogenic amines

BAs are basic nitrogen compounds with a low molecular weight that are metabolized by the normal physiological function of microorganisms, plants, and animals. In food and beverages, enzymatic activity on proteins and amino acids of raw materials and amination of aldehydes and ketones are responsible for the formation of BAs, although the main source of these compounds is the microbiological activity and amino acid decarboxylation [16]. Small amounts of BAs have a role in the normal physiology of living organisms, while the intake of high levels of BAs can produce toxic or adverse effects on human health, such as allergies, gastrointestinal and/or vascular disorders [17], being able to cause more serious diseases such as cancer and even death. BAs are found in many foods and beverages, including meat, fish, vegetables, fruits, and dairy products.

Due to the high impact that gases have on food quality and safety, many different approaches have been carried out to develop intelligent polymers to detect them. Most of these smart polymers have been developed to be included in food packaging systems whose response can be easily observed through optical changes, although they also exist with an electrochemical response. Increased CO_2 levels in packaged foods can be detected directly or indirectly by smart polymers in combination with pH-responsive dyes. Natural polymer-based coatings containing different mixtures of pH-sensitive dyes (bromothymol blue, methyl red, bromocresol green, and/or phenol red) responds to changes in CO_2 concentration since their presence lowers the pH [18]. Although they are not strictly smart polymers, since the polymer is not the one with the sensing ability but the dye, we have included them here, because they are very commonly used as food quality indicators. A relevant approach is the use of an intelligent polymer that modifies its transparency with increasing the concentration of CO_2 [19]. When CO_2 is dissolved in water, it forms carbonic acid, lowering the pH, which modifies the opacity of the chitosan-based polymer. In general, common strategies to measure CO_2 to control food quality are based on a pH change, and further discussion can be found in this sense later in this chapter.

In addition, most smart polymers developed for O_2 sensing have been based on redox-type reactions using LDPE polymers and redox dyes such as methylene blue [20]. However, intelligent polymers also detect O_2 in commodity plastic films by treating PE/PP polymer films with a solvent crazing process to form nanometric pores in a well-defined network and filling the pores with a sensor that changes its color in the presence of O_2[21].

The main smart polymers developed to detect VOCs are based on colorimetric detection methods using pH-dye indicators that react with the chemical compounds released by the microbial activity in food spoilage. One of the most used strategies consists of the entrapment or dispersion of pH-sensitive molecules in a film in which a color change occurs due to the halochromic nature of the indicators that open or close their sulfoxide ring in the presence of OH^- or H^+ [22]. These types of intelligent polymers are highly sensitive to the presence of basic nitrogen compounds such as trimethylamine, dimethylamine, and ammonia in seafood products. In addition, intelligent polymers can be developed to monitor fresh milk following a similar approach.

Due to their basic nature, most of the BAs sensors developed are also based on pH indicators dispersed in polymeric films. Moreover, smart polymers with color response have also been used for the detection of BAs such as histamine, putrescine, cadaverine, or tyramine, among others. For example, acrylic and aramid smart polymers (films or coated textiles) containing sensory motifs have been developed, which suffer a color change when interacting with BAs in the gas phase in beef or tuna. The sensing mechanism is based on the formation of Meisenheimer complexes in the acrylic polymers or through a nucleophilic substitution in the aramid sensing motifs [23,24]. Another interesting alternative is the use of PANi films as chemical sensors to monitor fish spoilage through a color variation from green to blue due to a pH increase as a response to the BAs release [25].

Commercial food freshness indicators related to fish or meat spoilage can also be found. For example, Senso Q^{TM} (DSM), based on anthocyanins dispersed in a polymer matrix, was used to determine BAs in fish and poultry. Unfortunately, this one was not commercially successful, and the same authors developed a new colorimetric sensor, Raflatac. This time the sensor based on a silver nanolayer (brown and opaque) turns transparent when silver sulfide is formed after reacting with hydrogen sulfide (decomposition of cysteine) [26].

On the other hand, it is important to highlight that enzyme-based sensory polymers have been developed to detect BAs in combination with an electrochemical response using conducting polymers, providing a simple, rapid, and very sensitive solution to quantify them [27]. One typical useful response when using conducting polymers (PAni, PEDOT or PPy) is electrical resistance when the smart polymer interacts with the target analyte. Gaseous species like NH_3, H_2S, CO, CO_2, alcohols, or environmental humidity are usually detected using resistive techniques [28]. In addition, the use of MIPs in combination with electrochemical sensors is also applied to detect different BAs. This polymer-electrode smart disposition allows performing electrochemical measurements and is the most widely used voltammetry [29].

Despite the large number of smart polymers developed to detect different gaseous indicators, further research is still needed because there are still molecules that we cannot distinguish because they are very similar to each other by these intelligent polymers. For example, differentiating the levels of methanol from ethanol in beverages such as wine samples using a smart polymer is still a challenge.

3.2. Humidity, temperature, and pH

Food is drastically affected by sudden temperature, humidity, and pH changes. Generally, alterations in one of these parameters produce modifications in another since they are closely related, especially in packaged products. Therefore, the control and monitoring of these parameters during the food production and distribution chain is essential to guarantee food quality and safety.

Food temperature control from the production process to the consumer's arrival is a critical parameter affecting food spoilage since temperature determines the storage time. Variations in the temperature during the food distribution chain trigger microbiological activity, decreasing the shelf life, and boosting food waste with an important economic impact. Time-temperature control during food distribution is important since breaks in the cold chain cause an increase in bacterial growth, loss of nutrients, protein denaturation or carbohydrate fermentation, among others, leading to food safety issues, and sensory attributes, especially important for dairy products, meat and fish products, and vegetables [4,13].

Also, an optimal humidity degree is needed for preserving the food quality and shelf life of products. For instance, fresh-cut fruit and vegetables require high relative humidity to maintain food properties and avoid weight loss, although these high humidity levels trigger a rapid microorganism and fungi growth. In addition, the type of materials used for food packaging has a key role in its permeability and sorption characteristics for controlling humidity [4,30].

Regarding the pH, most food shows a pH between 3.5 and 7 and directly affects the food pigments (responsible for fruit, vegetables, and meat color) and the food texture (associated with the fish and meat muscles pH). Modifications in food environmental pH are directly related to the metabolic activity of microorganisms, indicating microbial proliferation and food spoilage. These metabolites can be liquids or gases, such as lactic acid, acetic acid, volatiles, or CO_2, which decrease the environmental pH once dissolved. So, identifying and knowing the pH of the food and maintaining it at its normal values is critical to producing and consuming safe and healthy products [4,13]. The detection of changes in pH using smart polymers has been carried out mainly by pH-dye polymers as mentioned in the gas indicator section due to both gas and pH indicators are closely related.

Thermo-responsive polyurethanes (TSPU) can control vapor permeation through the phase transition temperatures. They can be used as packaging materials since they exhibit close-open behavior of the free volume holes as a function of the temperature. Below the phase transition temperature, the polymer chains are frozen and in a glassy state, and the free volume holes are very small. When the temperature increases, chains can move, and the free volume holes increase their size, changing the breathability and water vapor transmission, and thus, the humidity [31]. In addition to changes in volume, TSPU nanofibers can be deposited over a PET nonwoven nanofiber mat. The material is opaque when refrigerated and becomes irreversibly transparent at room temperature. This change in the optical properties reveals a hidden warning alert behind the TPU [32].

Also, dual responsive materials can be prepared, e.g., temperature and pH-responsive. A typical thermo-responsive material is poly(*N*-isopropylacrylamide) (PNIPAM), having both hydrophilic and hydrophobic side groups. When the temperature increases, the hydrophobic interactions dominate over the hydrophilic, collapsing the polymeric structure. This fact is used to encapsulate substances, to be released as the temperature rises in the food package. One of these substances can be pimaricin, with antifungal properties. If a hydrophilic monomer such as acrylic acid is included in the formulation of PNIPAM, the material is responsive both to the temperature and the pH, with a higher degree of collapse at low pH [31].

3.3. Microorganisms

Microorganisms are sometimes used to process some foods, but they are probably the most important food quality and safety indicator. Although microorganisms' detection methods are highly sensitive and reliable, they are usually time-consuming, require qualified personnel, and in some situations, show problems in the identification of specific microorganisms [33]. Microorganisms present in food can be part of the food's flora (associated with microbial quality and food spoilage), or pathogenic microorganisms of external origin that show up after poor handling or contamination of the food product [4].

Pathogenic microorganisms are the main cause of illness and death from food poisoning, so their detection is essential for public health. Pathogenic microorganisms include bacteria (*Escherichia coli*, *Listeria monocytogenes* or *Salmonella* spp.), viruses (*Hepatitis A viruses, Noroviruses*), parasites (*Cyclospora cayetanensis*, *Toxoplasma gondii*), yeast (*Candida alimentaria*, *Pichia fermentans*) and molds (*Aspergillus flavus*, *Penincillum expansum*) and they can be found in meat, seafood products, dairy products, and water. Moreover, these microorganisms can produce serious illnesses due to their rapid growth and colonization of new niches inside the human body, and they can produce hazardous mycotoxins for human health [34].

Polymeric biosensors that respond to pathogenic microorganisms are very specific but still challenging for researchers. There are some examples of the use of smart polymers based on the covalent binding of highly specific ligands to polymeric matrices. These ligands are molecules (antibodies, peptide ligands, enzymes, aptamers...) that specifically recognize other molecules present in microorganisms such as proteins or polysaccharides or even their genetic material. One of the first commercialized smart polymers to detect pathogenic microorganisms was Toxin Guard^{TM} (Toxin Alert, Canada), which is prepared by immobilizing different antibodies onto a flexible polyethylene packaging. This sensor is an example of a unique composite material capable of detecting and identifying multiple biological materials in a single package, such as *Salmonella* sp., *Campylobacter* sp., *E. coli,* and *Listeria* sp., using a distinctive icon to visually identify the biological material through conjugated dyes, photoactive compounds, etc. [35]. More recently, a cyclo-olefin polymer with a covalently attached RNA-cleaving fluorogenic DNAzyme probe can detect the presence of *E. coli* colonies in meat and juice by emitting a fluorescent signal [36]. Other commercial strategies with less success were also based on colorimetric indicators (FreshTag®), or biosensors in the barcode to detect pathogens (Sentinel System^{TM}). In addition, some MIPs have also been described for the specific detection of these microorganisms [29].

Responsive materials also find application in food packaging by encapsulating active components with antimicrobial activity, vitamins, or antioxidants. Normally these active compounds are released through variations in the swelling and water uptake of the films. However, they are not extensively used due to a lack of consistency with the extrapolated results from the laboratory to the industry, based on the use of food simulants in the former, while the latter contains more salts, lower water activity, nutrients, proteins, and fats, that interact with the released encapsulated components [37].

3.4. Miscelanea

3.4.1. Chemicals derived from pesticides

According to the European Commission, a pesticide is "something that prevents, destroys or controls a harmful organism (pest) or disease, or protects plants or plant products during their production, storage, and distribution". This term includes herbicides, insecticides, fungicides, acaricides, molluscicides, nematicides, growth regulators, and repellents, among others [38].

For years, pesticides have increased crop yields to feed the world's population. However, their improper, abusive and uncontrolled use cause the emergence of very harmful residues for humans and other living beings, mainly in drinking water. Human exposure to these pesticide residues causes headaches, neurotoxicity, respiratory distress, chronic diseases, cancer, or death [39]. Because of this, the European Commission in the 396/2005 regulation, established the maximum limits of pesticide residues that can be found in food, and it also presents an annual report evaluating the levels of these residues in the European marketed food, finding several non-accepted pesticides of illegal use in high values. Pesticide residue levels above the established limits have also been identified, especially in spinach [40]. Identification and detection of pesticide residues are complex due to the high amount of chemical pesticide derivatives and the time-consuming techniques.

Recently, MIPs are finding applications for the determination of pesticides. MIPs allow both the pre-concentration and purification of the sample and the extraction of the pesticide from the media in a selective manner, which is very important when interferents are present affecting the determination. The use of MIPs in water quality control serves for *in-situ* monitoring of carbofuran, or organophosphorus pesticides such as diazinon in combination with other electrochemical techniques such as cyclic voltammetry or impedance measurements [41]. Other interesting analytical procedures include the coating of paper with MIPs and the use of colorimetry or fluorescence to visually observe the presence of pesticides in fruit such as tomatoes and apples [42].

Also, biosensors based on enzymes immobilization in a polymeric matrix in screen-printed electrodes are raised as real-time analytical systems for pesticides, specially dichlorvos and methylparaoxon in aqueous matrices [9].

3.4.2. Nitrates and nitrites in water

Industrial manufacturer and agriculture runoff primarily cause nitrate and nitrite water contamination. When consumed in drinking water, both nitrates and nitrites are rapidly absorbed by the digestive system, distributed along the human body, and finally excreted in the urine. However, higher doses of these compounds can cause methemoglobinemia (hemoglobin oxidation by nitrite inhibiting the normal oxygen transport across the organism), producing cyanosis and asphyxia. Furthermore, nitrates and nitrites can cause cancer and effects the thyroid system [43].

MIPs-modified electrodes are also being used to determine many compounds in water and food, including nitrates. MIPs (ion-imprinted polymers particularly) have been used as a coating to develop a low-cost sensor with selective recognition combined with other techniques such as electrochemical impedance spectroscopy to measure nitrate in water [44].

3.4.3. Heavy metals

Heavy metals (Hg, Cd, Pb, Cr, As…), mainly derived from atmospheric deposition, industrialization, and intensive agricultural practices, contaminate the soil and water and are absorbed by crops, thus passing into the food chain. All these pollutants seriously affect health by causing metabolic disorders and affecting the physiological function of the organs. Various polymeric materials have been described for the detection of heavy metals in aqueous media, mainly with an optical response [45]. Acrylic-based polymers can detect by a colorimetric change and eliminate Hg (II) in seafood and water [46]. In addition, as adsorbents, both pH and temperature-responsive polymers have proven to be effective in removing heavy metals in water as a function of the pH of the media, both for domestic used and for wastewater treatment. A variation in the pH or the temperature results in variations in the filtration ability through an alteration of their pore sizes and flux through shrinking and swelling, and even the possibility to separate oil from wastewater. Also, these polymeric materials can change their working mechanism triggered by the nature and concentration of an electrolyte/salt ion in the surroundings through the control of the pore conformation [47].

3.4.4. Other food quality parameters

There are other substances present in food and not necessarily harmful to humans that guarantee food authenticity or provide beneficial qualities. Polyphenols are an important example and are present in different foods such as fruits, vegetables, and beverages derived from them and have antioxidant and antimicrobial activities. Intelligent polymers capable of detecting this type of compound have also been developed by a colorimetric response using acrylic-based smart polymers [48]. Furthermore, halal verification can be performed by using a naked-eye ethanol PANi biosensor. Alcohol oxidase is immobilized onto PANi, and when alcohol reacts with it, a color variation from green to blue is produced due to the release of acetaldehyde and hydrogen peroxidase, which oxidizes PANi [26].

4. CONCLUSIONS AND FUTURE PERSPECTIVES

Food quality analytical tools are currently expensive, require specialized personnel, are time-consuming, and are not readily available for *in-situ* and real-time evaluation. On the other hand, smart polymers can be a key tool to reduce diseases and food waste, since they allow the determination of food quality indicators in a fast, easy, simple, and cheap way. Additionally, they can avoid food adulteration, and improve the distribution chain's knowledge during storage and transportation. Although these systems can open a revolutionary approach in food packaging and in measuring techniques, some major factors still need to be considered, as observed in the limited number of commercialized systems. In this sense, research directed this way will provide industries, consumers, and regulatory authorities acceptance, environmental effectiveness, and economic benefits, by decreasing foodborne illnesses and food waste and contributing to a more sustainable world.

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REFERENCES

[1] O.A. Odeyemi, N.A. Sani, A.O. Obadina, C.K.S. Saba, F.A. Bamidele, M. Abughoush, A. Asghar, F.F.D. Dongmo, D. Macer, A. Aberoumand, Food safety knowledge, attitudes and practices among consumers in developing countries: An international survey, Food Res. Int. 116 (2019) 1386–1390.

[2] J. Gustavsson, C. Cederberg, U. Sonesson, R. V. Otterdijk, A. Meybeck, Global food losses and food waste – Extent, causes and prevention, Food Agric. Organ. United Nations. Rome; 2011.

[3] A.M. Giusti, E. Bignetti, C. Cannella, Exploring New Frontiers in Total Food Quality Definition and Assessment: From Chemical to Neurochemical Properties, Food Bioprocess Technol. 1 (2008) 130–142.

[4] H. Yousefi, H.-M. Su, S.M. Imani, K. Alkhaldi, C.D. M. Filipe, T.F. Didar, Intelligent Food Packaging: A Review of Smart Sensing Technologies for Monitoring Food Quality, ACS Sensors 4 (2019) 808–821.

[5] J.M. García, F.C. García, J.A. Reglero Ruiz, S. Vallejos, M. Trigo-López, Smart Polymers. Principles and Applications, De Gruyter; 2022.

[6] M. Wei, Y. Gao, X. Li, M.J. Serpe, Stimuli-responsive polymers and their applications, Polym. Chem. 8 (2017) 127–143.

[7] Q. Lin, Y. Li, M. Yang, Polyaniline nanofiber humidity sensor prepared by electrospinning, Sensors Actuators B Chem. 161 (2012) 967–972.

[8] M. Khadem, F. Faridbod, P. Norouzi, A. Rahimi Foroushani, M.R. Ganjali, S.J. Shahtaheri, R. Yarahmadi, Modification of Carbon Paste Electrode Based on Molecularly Imprinted Polymer for Electrochemical Determination of Diazinon in Biological and Environmental Samples, Electroanalysis 29 (2017) 708–715.

[9] I. Yaroshenko, D. Kirsanov, M. Marjanovic, P.A. Lieberzeit, O. Korostynska, A. Mason, I. Frau, A. Legin, Real-Time Water Quality Monitoring with Chemical Sensors, Sensors 20 (2020) 3432.

[10] K.B. Biji, C.N. Ravishankar, C.O. Mohan, T.K. Srinivasa Gopal, Smart packaging systems for food applications: a review, J. Food Sci. Technol. 52 (2015) 6125–6135.

[11] R. Ahvenainen, Active and intelligent packaging, In: Ahvenainen R, editor. Nov. Food Packag. Tech. Cambridge: Woodhead Publishing; 2003. p. 5–21.

[12] M. Smolander, Freshness Indicators for Food Packaging, In: Kerry J, Butler P, editors. Smart Packag. Technol. Fast Mov. Consum. Goods John Wiley & Sons, Ltd; 2008. p. 111–127.

[13] M. Weston, S. Geng, R. Chandrawati, Food Sensors: Challenges and Opportunities, Adv. Mater. Technol. 6 (2021) 2001242.

[14] M. Loughran, D. Diamond, Monitoring of volatile bases in fish sample headspace using an acidochromic dye, Food Chem. 69 (2000) 97–103.

[15] R.J. Mcgorrin, The Significance of Volatile Sulfur Compounds in Food Flavors An Overview, Volatile Sulfur Compd. Food American Chemical Society; 2011. p. 3–31.

[16] Y. Özogul, F. Özogul, Chapter 1 Biogenic Amines Formation, Toxicity, Regulations in Food, Food Chem. Funct. Anal. (2019) 1–17.

[17] D. Doeun, M. Davaatseren, M.S. Chung, Biogenic amines in foods, Food Sci. Biotechnol. 26 (2017) 1463–1474.

[18] C. Rukchon, A. Nopwinyuwong, S. Trevanich, T. Jinkarn, P. Suppakul, Development of a food spoilage indicator for monitoring freshness of skinless chicken breast, Talanta 130 (2014) 547–554.

[19] J. Jung, P. Puligundla, S. Ko, Proof-of-concept study of chitosan-based carbon dioxide indicator for food packaging applications, Food Chem. 135 (2012) 2170–2174.

[20] A. Mills, K. Lawrie, J. Bardin, A. Apedaile, G.A. Skinner, C. O'Rourke, An O2 smart plastic film for packaging, Analyst 137 (2011) 106–112.

[21] R.N. Gillanders, O. V. Arzhakova, A. Hempel, A. Dolgova, J.P. Kerry, L.M.

Yarysheva, N.F. Bakeev, A.L. Volynskii, D.B. Papkovsky, Phosphorescent Oxygen Sensors Based on Nanostructured Polyolefin Substrates, Anal. Chem. 82 (2010) 466–468.

[22] B. Liu, P.A. Gurr, G.G. Qiao, Irreversible Spoilage Sensors for Protein-Based Food, ACS Sensors 5 (2020) 2903–2908.

[23] J.L. Pablos, S. Vallejos, A. Muñoz, M.J. Rojo, F. Serna, F.C. García, J.M. García, Solid polymer substrates and coated fibers containing 2,4,6-trinitrobenzene motifs as smart labels for the visual detection of biogenic amine vapors, Chem. - A Eur. J. 21 (2015) 8733–8736.

[24] L. González-Ceballos, B. Melero, M. Trigo-López, S. Vallejos, A. Muñoz, F.C. García, M.A. Fernandez-Muiño, M.T. Sancho, J.M. García, Functional aromatic polyamides for the preparation of coated fibres as smart labels for the visual detection of biogenic amine vapours and fish spoilage, Sensors Actuators B Chem. 304 (2020) 127249.

[25] B. Kuswandi, Jayus, A. Restyana, A. Abdullah, L.Y. Heng, M. Ahmad, A novel colorimetric food package label for fish spoilage based on polyaniline film, Food Control 25 (2012) 184–189.

[26] E. Poyatos-Racionero, J.V. Ros-Lis, J.-L. Vivancos, R. Martínez-Máñez, Recent advances on intelligent packaging as tools to reduce food waste, J. Clean. Prod. 172 (2018) 3398–3409.

[27] K. Mitsubayashi, Y. Kubotera, K. Yano, Y. Hashimoto, T. Kon, S. Nakakura, Y. Nishi, H. Endo, Trimethylamine biosensor with flavin-containing monooxygenase type 3 (FMO3) for fish-freshness analysis, Sensors Actuators, B Chem. 103 (2004) 463–467.

[28] J. Reglero Ruiz, A. Sanjuán, S. Vallejos, F. García, J. García, Smart Polymers in Micro and Nano Sensory Devices, Chemosensors 6 (2018) 12.

[29] D. Elfadil, A. Lamaoui, F. Della Pelle, A. Amine, D. Compagnone, Molecularly Imprinted Polymers Combined with Electrochemical Sensors for Food Contaminants Analysis, Molecules 26 (2021) 4607.

[30] V. Siracusa, Food Packaging Permeability Behaviour: A Report, Int. J. Polym. Sci. 2012 (2012) 11.

[31] S. Purkayastha, A.K. Biswal, S. Saha, Responsive Systems in Food Packaging, J. Packag. Technol. Res. 1 (2017) 53–64.

[32] S. Choi, Y. Eom, S. Kim, D. Jeong, J. Han, J.M. Koo, S.Y. Hwang, J. Park, D.X. Oh,

A Self-Healing Nanofiber-Based Self-Responsive Time-Temperature Indicator for Securing a Cold-Supply Chain, Adv. Mater. 32 (2020) 1907064.

[33] J.W.F. Law, N.S.A. Mutalib, K.G. Chan, L.H. Lee, Rapid methods for the detection of foodborne bacterial pathogens: Principles, applications, advantages and limitations, Front. Microbiol. 5 (2014) 770.

[34] T. Bintsis, Foodborne pathogens, AIMS Microbiol. 3 (2017) 529–563.

[35] W.T. Bodenhamer, Method and apparatus for selective biological material detection (US6051388A), United States; 1999.

[36] H. Yousefi, M.M. Ali, H.M. Su, C.D.M. Filipe, T.F. Didar, Sentinel Wraps: Real-Time Monitoring of Food Contamination by Printing DNAzyme Probes on Food Packaging, ACS Nano 12 (2018) 3287–3294.

[37] B. Malhotra, A. Keshwani, H. Kharkwal, Antimicrobial food packaging: potential and pitfalls, Front. Microbiol. 6 (2015) 611.

[38] European Commission. Food Safety. Pesticides [Internet],.

[39] V.L. Zikankuba, G. Mwanyika, J.E. Ntwenya, A. James, Pesticide regulations and their malpractice implications on food and environment safety, Cogent Food Agric. 5 (2019) 1601544.

[40] L. Carrasco Cabrera, P. Medina Pastor, The 2019 European Union report on pesticide residues in food, EFSA J. 19 (2021) 6491.

[41] A.R. Cardoso, A.P.M. Tavares, M.G.F. Sales, In-situ generated molecularly imprinted material for chloramphenicol electrochemical sensing in waters down to the nanomolar level, Sensors Actuators B Chem. 256 (2018) 420–428.

[42] M. Vodova, L. Nejdl, K. Pavelicova, K. Zemankova, T. Rrypar, D. Skopalova Sterbova, J. Bezdekova, N. Nuchtavorn, M. Macka, V. Adam, M. Vaculovicova, Detection of pesticides in food products using paper-based devices by UV-induced fluorescence spectroscopy combined with molecularly imprinted polymers, Food Chem. 380 (2022) 132141.

[43] World Health Organization, Nitrate and nitrite in Drinking-water. Background document for development of WHO Guidelines for Drinking-water Quality, Guidel. Drink. Qual. 2003. p. WHO/SDE/WSH/04.03/56.

[44] M.E.E. Alahi, S.C. Mukhopadhyay, L. Burkitt, Imprinted polymer coated impedimetric nitrate sensor for real- time water quality monitoring, Sensors Actuators B Chem. 259 (2018) 753–761.

[45] A.M. Sanjuán, J.A. Reglero Ruiz, F.C. García, J.M. García, Recent developments in

sensing devices based on polymeric systems, React. Funct. Polym. 133 (2018) 103–125.

[46] S. Vallejos, J.A. Reglero, F.C. García, J.M. García, Direct visual detection and quantification of mercury in fresh fish meat using facilely prepared polymeric sensory labels, J. Mater. Chem. A 5 (2017) 13710–13716.

[47] K. Dutta, S. De, Smart responsive materials for water purification: an overview, J. Mater. Chem. A 5 (2017) 22095–22112.

[48] S. Vallejos, D. Moreno, S. Ibeas, A. Muñoz, F.C. García, J.M. García, Polymeric chemosensor for the colorimetric determination of the total polyphenol index (TPI) in wines, Food Control 106 (2019) 106684.