

Classification of Advanced Polymers by Application in Food/Beverages

Subjects: Polymer Science

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Polymers are extensively used in food and beverage packaging to shield against contaminants and external damage due to their barrier properties, protecting the goods inside and reducing waste. In addition to protecting the edible goods inside any package, researchers in polymers for food and beverage applications have leapt to develop polymers for advanced applications.

Keywords: advanced food packaging ; polymer sensors ; active packaging

1. Introduction

Polymer science and technology is devoted to the development of materials with unique functionalities for packaging, construction, medical applications, electronics, or aeronautics due to their tunable nature and a wide variety of physical and chemical properties. Since their industrial development in the 1930s, polymers have been and will be a fundamental pillar of the food industry as we know it nowadays. The transport, storage, and conservation of practically all food products at a reasonable price is only possible due to a perfect balance between the mechanical properties of polymers, their price, low weight, and barrier effect against different gases. Traditional polymers used in food packaging applications include polyethylene (PE), polyethylene terephthalate (PET), or polystyrene (PS), among others. They serve as protection against chemical, biological, and physical damage and prevent the loss of aroma, flavor, and/or antioxidants. They ensure an adequate balance of gases and humidity inside the packaged food, increasing the shelf life of food and facilitating its handling ^{[1][2][3]}.

Current trends in food packaging go a step forward to serve as active packaging too, delivering chemical species such as antioxidants and antimicrobials in their polymer formulation that are released (or not) from the package to protect the goods inside and extend their shelf-life. Also, the use of edible polymers or biopolymers for food packaging is gaining interest for reducing waste. In addition to protecting the edible goods inside any package, researchers in polymers for food and beverage applications have leapt to develop polymers for advanced applications ^{[4][5][6][7][8][9][10][11][12][13][14][15]}. Such innovations are smart polymers for the detection of targets (chemical species, physical stimuli, microorganisms, etc.), extraction of contaminants, separation of compounds of interest, controlled release of species in active packaging, etc.

2. Classified by Application (Advanced Polymers)

2.1. Advanced Food Packaging

Food packaging is the main and best-known application of polymeric materials in the food industry. The global production of plastics is distributed mainly in packaging (42%), automotive (8%), construction (20%), and the domestic environment (30%). Polymers have made significant advances in terms of quality and food safety ^[16].

Food packaging has grown from a mere food protection objective during manipulation to advanced functionalities aiming to extend their shelf-life and improve the attractiveness of the goods for consumption. The food packaging industry has progressed from using single-layer films to very complex multilayer films made from different polymers prepared by the co-extrusion or lamination of up to 13 layers or even more. The range of polymers used for food packaging is not very extensive, being the most common PE (low-density polyethylene, LDPE; high-density polyethylene, HDPE; linear low-density polyethylene LLDPE, polypropylene (PP) polyamide (PA; PA6, PA66), PET, PS, polyvinyl alcohol (EVOH), polyvinylidene chloride (PVDC), polyvinyl acetate (PVAc), poly(ethylene-co-vinyl acetate) (EVA), polycarbonate (PC), polyvinyl chloride (PVC), and poly(ethylene-co-acrylic acid) (EAA). Among them, the most extensively used are PE, PP, PA, PS, PET, and PVC. The characteristics and properties of single-layer films for packaging were described in scientific

literature a long time ago. Despite not showing a wide variety, their combination into three or more layers, with the possibility of being repeated and the diversity of their fabrication methods, their design, and improvement are very complex. Each polymer has a function in a multilayer film, including gas/aroma barrier, scratch barrier, moisture barrier, mechanical and/or heat resistance, adhesiveness, printability, etc. On the other hand, the properties of multilayer films are a sum of the properties of the single components plus the synergic effects associated with the adhesiveness, the interfaces, and the addition of charges. However, despite the existing theoretical knowledge related to the materials' properties, the films' composition and the number and nature of the multilayers are just part of the know-how of the enterprises manufacturing them ^{[6][15][17][18][19]}.

2.1.1. Active Packaging through Chemical Species Release

The main goal of active packaging is to control the package headspace composition during the shelf life of the goods inside to reduce food waste. Active packaging is not a new concept (the first patents date back to the beginning of the 20th century). Still, the controlled release of substances to the media or the absorption of others to preserve food means a new generation of packaging. In fact, it is a very extensive field since different ingredients show different preserving mechanisms. Most of these mechanisms go through the improvement of antioxidant and antimicrobial activities. Using active packaging instead of directly adding the substances to the bulk of the food can diminish the amount of substance required, especially through a controlled release, since the degradation or bacterial growth of food takes place mainly on the surface. However, the complex structure of food can vary the releasing or absorption rates and thus the efficiency and activity of the packaging, limiting the widespread use of active packaging ^[20].

Many different polymers are used within this frame, like natural polymers such as gelatin, starch, and chitosan, or synthetic polymers, such as poly(lactic acid) (PLA) or PP, which are the most relevant ones ^[21].

2.1.2. Active Packaging without Chemical Species Release

Unlike active packaging with substances release, intrinsically antimicrobial polymers include the active ingredient in their chemical structure, showing essential advantages compared to the former: there is no migration of substances, and, therefore, the antimicrobial effect of the material is non-perishable, allowing the material to be reused. There are hardly any studies of intrinsically antimicrobial materials that are not based on the migration of a component whose bacterial inhibition values are reasonable and have been tested under real conditions.

González-Ceballos et al. used a copolymer of *N*-vinylpyrrolidone, methylmethacrylate, and a monomer with a covalently anchored vanillin derivative to prepare an antimicrobial absorbent food pad without the migration/delivery of substances ^[22]. The film-shaped pad was simply washable and reusable ten times at least, showing a shelf-life extension = 50%. The pads were tested in pork samples for *E. coli*, *S. aureus*, and *L. monocytogenes*, with inhibition up to 99.95%, 99.96%, and 99.02%, respectively. Delezuk et al. followed a different strategy. They used chitosan as the polymer, designing a micromotor-based bacteria-killing approach, relying on the combination of the inherent antimicrobial capacity of chitosan with the effective water-powered propulsion of magnesium micromotors, and showing a bacteria-killing efficiency of 96% within 10 min ^[23].

Furthermore, adding inexpensive fillers to the PLA matrix can lower costs, according to Spiridon et al. They studied formulations of PLA containing grape wastes and celery fibers to prepare composites with good mechanical and thermal properties and antimicrobial activity, appropriate for food-active packaging polymers, particularly when using grape waste ^[24].

2.1.3. Edible Polymers and Biopolymers

Edible polymers are biodegradable and biocompatible polymer formulations applied on food surfaces as films that prevent food deterioration by providing barrier properties and enhancing quality and safety ^[25]. The major difference between edible polymers and others used for food packaging is that the former becomes part of the food while the latter becomes waste. Edible polymers are generally applied as a coating on certain foods, but they can also be prepared as film-shaped materials and serve as packaging. These polymers improve and preserve food quality and can be both classic synthetic polymers and biopolymers. Still, the latter has more relevance nowadays since they are usually environmentally friendly, that is, biodegradable polymers obtained from natural resources (green polymers) ^{[26][27]}.

The use of these polymers in no case can compromise the quality of food, and their functions range from inhibiting lipid oxidation to diminishing metmyoglobin development in fresh meat. Edible films prepared from milk proteins (such as casein, lactoferrin, or whey protein) have proven to be a reliable and firm alternative to polymers derived from oil and used in food packaging ^{[28][29]}. Furthermore, these polymers can also be used for the controlled delivery of different substances,

such as preservatives, provided that they are included in the list of products accepted as food-grade [26]. Edible coatings, and especially those made with biopolymers, are a sustainable alternative that offers a wide range of possibilities in terms of functionality, such as barrier properties (low permeability to water vapor and oxygen) for totally protective food packaging [30].

Over the last few years, academic research has given relevant importance to polysaccharides for the manufacture of edible polymers and biopolymers for food packaging, which seems quite logical since they are biodegradable, not toxic, can be manufactured as films, are widely available in nature, and have good compatibility with cellulose-based supports [18]. However, they are polymers that are quite sensitive to humidity, which limits their use on a large-scale basis, as the main drawback. On the other hand, this also opens the door to new lines of research aimed at the chemical modification of polysaccharides and other natural polymers, introducing different additives in their formulations for improving mechanical and thermal properties, decreasing the permeability to water vapor, and increasing elongation at break, tensile, and antimicrobial properties [30][31].

Some of the properties of edible polymers can also be enhanced when combined with natural antimicrobial compounds. Piñeros-Hernandez et al. used polyphenol-rich rosemary extracts to introduce them into cassava starch films to prepare active food packaging with antioxidant capacity. The polyphenol content ranged from 4.4 to 13.6 mg of gallic acid equivalents per gram. In addition to enhancing the materials' antioxidant properties, other properties such as barrier protection against ultraviolet light, mechanical properties, permeability to water vapor, or hydrophobicity vary with the amount of rosemary extract added to the films [32]. In another example, Elsabee et al. described different strategies to improve the mechanical properties of an edible polymer, such as chitosan, a marine-available, biocompatible, biodegradable polysaccharide with antibacterial and antifungal properties. Some of these strategies are based on adding to chitosan other natural polymers, such as starch, essential oils, or clays [33].

Davachi et al. describe the natural polymer *salvia macrosiphon* seed mucilage and the enhancement of target properties by adding small amounts ($\approx 2\%$) of glycerol and nanoclays [31]. Jang et al. prepared edible polymers with high tensile strength using the residues generated in the rapeseed oil extraction process. These residues are rich in a major protein comprised of two polypeptide chains, α , and β , of 20 kDa and 30 kDa, linked by a disulfide bond. The film-forming solution was prepared with the residues, plasticizers (sorbitol and sucrose), emulsifiers (polysorbate), and gelatin (*gelidium corneum*) [34].

2.2. Target Species Detection and Quantification (Sensory Polymers)

Food control and safety are among the most critical areas in the food industry. In this framework, polymers, specifically smart polymers, have been a great revolution in the last decade because of their low costs, ease of use, and versatility in adapting to any target species [19]. A smart polymer is defined as a polymer that, through a specific mechanism, offers a response to a specific stimulus. Therefore, these polymers can be classified by the stimulus (chemical or physical), by the signal transduction mechanism (conducting polymers, molecularly imprinted polymers (MIPs), dosimeters, indicator displacement assays or IDAs, etc.), or by the response (colorimetric, fluorometric, electrical, etc.). However, a key concept defines sensory polymers: the response is an alert. In other words, smart polymers are divided into responsive polymers or sensory polymers if they respond with an action (drug delivery, change in size or shape, etc.) or with an alert, respectively [35].

Among the sensory polymers in food applications, the most relevant are classified based on the following targets: drugs, smell and taste, biogenic amines, heavy metals, humidity and gases, temperature and pH, nitrates and nitrites, and microorganisms, among others.

2.2.1. Drugs

Human beings release different drugs into the environment through the biological waste generated or through a deficient wastewater purification process. These compounds are not adsorbed in the subsoil and end up in underground aquifers. Therefore, they pose a serious environmental problem that has aroused scientific interest in different fields, especially in drinking-water control and monitoring.

Undeniably, antibiotics are one of the most sought-after and controlled targets. Xiao et al. designed 3D polymer slides based on polylysine to detect cephalosporins, aminoglycosides, and sulfonamide antibiotics in pork and milk. However, the detection of antibiotics has also attracted the scientific community's attention. Madikizela et al. describe a MIP for the solid-phase detection of nonsteroidal anti-inflammatory drugs such as naproxen, ibuprofen, and diclofenac [36]. MIPs are synthetic polymers with unique molecular recognition capabilities showing high selectivity for target species by mimicking

the interactions taking place in natural receptors (such as antigen–antibody) but without stability restrictions. The detection system based on MIPs is complemented by a high-resolution liquid chromatograph equipped with photodiode array detection. As a result, limits of detection of 0.15, 1.00, and 0.63 $\mu\text{g L}^{-1}$ were reached for naproxen, ibuprofen, and diclofenac, respectively, and the most abundant drug of all in the different analyzed samples was ibuprofen, sometimes reaching concentrations higher than 220 $\mu\text{g L}^{-1}$. In fact, MIPs are one of the most broadly used polymers in this section, and other authors have described sensory polymers for the detection of tetracycline drugs in animal-derived foods [37] or the determination of streptomycin residues in food [38], among others [39].

Another type of polymer chosen by many authors to prepare sensory polymers for drug detection are conductive polymers. Karaseva et al. designed a sensory polymer based on polypyrrole to detect trace quantities of chloramphenicol, a veterinary drug for treating and preventing infectious diseases [40]. Similar systems can be found in the literature for 6-mercaptopurine detection (an anticancer drug used to treat leukemia) or piroxicam detection (a nonsteroidal anti-inflammatory drug) [41].

2.2.2. Smell and Taste

In industrial sectors, such as the food or even the automotive industry, aromas are evaluated by a group of skilled panelists through sensory analysis. The human nose and tongue can recognize millions of odors/tastes with a precision that no other analytical instrument has been able to reach up to date.

However, these analyses are always associated with human errors, such as individual variability. Electronic nose systems (e-nose) are a suitable alternative for scent recognition. These systems are made up of one or several chemical sensors capable of reacting with different gases and emitting a measurable signal. These systems produce a huge amount of data, so they are usually complemented with advanced mathematical procedures for data processing [42].

For this reason, the efforts of the scientific community to create e-noses and tongues are enormous since objectively determining tastes instead of using subjective sensory assessment and developing novel synthetic flavors in the food and beverage industry can be an advantageous methodology. Furthermore, polymers play a relevant role since the choice of the type of polymer and the method to integrate them into the systems (deposition, coating, etc.) directly affect the sensor's performance. Thus, many authors have generated excellent results over the last decade, as summarized herein.

Ahn et al. have developed an e-tongue for umami and sweet taste based on nanovesicles immobilized on poly(D-lysine) [43]. Related to milk analysis, Tazi et al. developed an e-tongue made of PVC but comprising a matrix of 16 different lipid/polymer membranes and performed a proof of concept by monitoring the flavor evolution in milk samples [44]. Additionally, Pérez-González et al. preferred to rely on PVC for the preparation of their e-tongue, which detected various compounds typically present in milk, including salts (CaCl_2 , KCl, and NaCl), sugars (galactose, glucose, and lactose), lactic acid, and organic acids such as citric acid [45].

This approach has also been applied to fruits, such as oranges. Gruber et al. designed an e-tongue based on four conducting polymers, poly(9,9-dioctyl-2,7-fluorenyleneethylen), poly(2,5-biphenyleneethylen), poly(4'-hexyloxy-2,5-biphenyleneethylen), and poly(2-bromo-5-hexyloxy-1,4-phenylenevinylene). The device can detect *Penicillium digitatum*, an important pest in all citrus-producing countries [46].

Some food additives, such as sugar, have also been the subject of research with e-noses. Péres et al. designed a low-cost chemoresistive gas sensor from a thin film of poly(2-dodecanoylsulfanyl-*p*-phenylenevinylene), a conductive polymer doped with dodecylbenzenesulfonic acid, and applied their development to the determination of methanol in sugar-cane spirit [47].

In another relevant investigation, Mahato et al. analyzed five bottled-water samples with three different e-tongues based on three functionalized polymer membrane electrodes: phosphorylated and crosslinked polyvinyl-co-ethylene membrane, phosphorylated hexadecyl trimethyl ammonium chloride modified EVOH-polyacrylic acid membrane and phosphorylated and crosslinked EVOH membrane. After analyzing the results, the authors concluded that the system could detect dissolved minerals in tested samples [48].

2.2.3. Biogenic Amines

Biogenic amines (BAs) are formed during the oxidative decarboxylation of the amino acids present in food caused by the breakup of proteins by microorganisms. Thus, they are generated in some foods' aging or decomposition processes, mainly fish, although their detection in cheeses is also of great importance [19]. These organic compounds are well-established indicators of food freshness and can cause severe harm to organisms after excessive intake. Most BAs,

except histamine, have high vapor pressure and can be detected in the gas phase. The most studied and abundant BAs in fish spoilage processes are tryptamine, histamine, trimethylamine, putrescine, 2-phenylethylamine, cadaverine, spermidine, spermine, tyramine, 1,7-diaminoheptane, and 1,6-diaminohexane.

In general, many of the investigations devoted to detecting the presence of BAs do not differentiate between specific amines since all kinds of BAs are formed in the deterioration of food. However, the BA detection mechanisms and the strategies followed are quite diverse. For example, for the detection of biogenic amines, Yuroba et al. prepared cellulose acetate electrospun nanofibers doped with the amine-reactive chameleon dye Py-1. Upon contact with BAs, the nanofiber mat converts the weak fluorescent pyrylium dye Py-1 into a pyridinium dye strongly emitting red [49]. Another strategy takes advantage of dopamine polymerization since this polymerization is very sensitive to BAs, indicating their presence [50].

Further, some examples of one single BA as the target species can be found in the literature. Vasconcelos et al. were able to detect putrescine using EVA containing maleic anhydride. Putrescine binds the maleic anhydride, triggering the resultant swelling of the polymer with spectral variations from an optical point of view [51]. Kumar and coworkers detected cadaverine, in addition to putrescine, with a poly(neutral red) electrochemical sensor. The positively charged groups on the polymer surface form ion-pair complexes with cadaverine or putrescine through diphosphate ion bridging, facilitating the detection and the formation of ion-pair [52]. Trimethylamine (TMA) was also solely detected using a copolymer of 2-hydroxyethyl methacrylate, 2-ethoxyethyl methacrylate, and an occluded pyrylium salt in the polymeric films, able to react with BAs, producing a unique change of color in the presence of TMA vapors [53].

As mentioned, histamine is the most challenging BA to be detected due to its low vapor pressure. However, Akhoundian et al. and Mattson et al. were able to detect it using MIP based on polymethacrylic acid incorporated into a carbon paste electrode [54][55].

2.2.4. Heavy Metals

Heavy metals have always been one of the most investigated contaminants due to their presence in water and various foods and their high toxicity to humans and the environment. Among the heavy metals, mercury is undoubtedly one of the most relevant, although sensing metals, including arsenic, cadmium, nickel, or lead, are also of great importance [56].

These metals reach the aquifers and the oceans through the pollution generated by combustion engines, brake pads, and emissions from industry, among others. Once in the environment, they are assimilated and bioaccumulated by organisms and pass into the food chain, directly affecting humans, so many research articles can be found concerning the detection of metals in fish.

2.2.5. Temperature and pH

Temperature sensors are very relevant in the food sector, especially in packaging. Keeping the cold chain is essential in transporting and storing refrigerated and frozen foods, such as fish, fruit, meat, etc. The great beneficiary of these sensors is always the final consumer, who receives information on the entire cold chain in the container, for example, with a colorimetric label. However, in general, neither the collecting/manufacturing companies, the transport companies, nor the markets are interested in this type of label since it brings to light errors in the food chain for which nobody wants to be held responsible. For this reason, temperature indicators are becoming more advanced and can indicate the exact moment when the cold chain was broken, namely, time-temperature indicators (TTIs). These systems are smart packaging devices that can monitor and reveal food quality loss through visualized information [57].

Sometimes, dual sensors are used to reach better systems, as in the study by Maddali et al., in which dual-mode temperature sensors are described [58]. The system is based on doped (oxidized) regiorandom poly(3-hexylthiophene), and a noticeable color variation from the doped state (blue) to the dedoped state (yellow) takes place when exposed to temperature. Furthermore, the colorimetric response can be complemented with the electrical signal, as doped films are electrically conductive. This combination leads to a sensory system with the broadest sensing range of any polymer-based temperature sensor described until today (from 30 to 75 °C). Although the authors did not perform a proof of concept with food, the temperature-sensing window aligns with food-packaging applications.

The waste generated by food packaging is one of the significant concerns of contemporary society. For this reason, many authors have begun to base polymeric sensors for temperature control on compostable polymers. For example, Salvatore et al. used a compostable and commercially available polymer (Ecoflex®, by BASF) to prepare biodegradable and extremely deformable temperature sensors for the internet of things [59].

In addition to temperature control, pH control is highly relevant in the food industry, specifically in certain foods. When some pathogenic microorganisms multiply, there is a change in the pH of the medium. Therefore, the control and monitoring of the pH is a marker for the preparation of polymeric sensors indicating the real state of the food to the consumer to avoid possible intoxication.

Some polymeric pH sensors are based on combinations of natural components such as *Euterpe oleracea* extract with polymers such as polycaprolactone (PCL) and polyethylene oxide [60]. Natural polymers are increasingly present in more products, and sensory polymers are no exception. For example, chitosan is not a polymer that responds to pH by itself, but it is an excellent support/matrix to house compounds such as phenol red or rosolic acid, providing materials with applications in food safety and biomedicine [61]. These types of sensors based on compounds or polymers of natural origin are the alternative to other polymeric sensors, such as those based on metal particles. For example, sensors prepared with polydiallyldimethylammonium [62] or polyimide [63], to which iridium oxide (IrO_x) nanoparticles are added.

However, only a few dual systems for pH and temperature (2 in 1) based on polymers and with proven applications in food safety have been reported. Among them, it is worth mentioning the study performed by Fucinõs et al. using poly(*N*-isopropylacrylamide) and poly(acrylic acid) [64] or the research by Topasna et al. using polyallylamine hydrochloride [65].

2.2.6. Humidity, Gases, and Other Volatile Substances

The control of diverse volatile substances in food is especially relevant for food preservation. For example, humidity can cause various pathogens to proliferate, resulting in food spoilage. Therefore, different humidity control strategies were followed, including preparing materials with PVP combined with azo dyes, Disperse Red 1 (DR1), and 4-diethylamino-4'-nitrozobenzene (DEA). This way, an easy and accessible way to produce humidity memory material that can be painted onto a variety of surfaces and shows a noticeable color change was enabled [66]. In another study, a conductive polymer (PEDOT:PPS) was applied to assess air quality, in the monitoring of the preservation state of foods, in the protection of walls, and even in wound-healing monitoring [67]. Similarly, for the control of humidity and aromas (apple, strawberry, and grape) added to gummy candies in the range of parts-per-billion, an e-nose based on polyaniline (PAni) was used, with limit of detection (LOD) in the range of ppb [68].

Conductive polymers were also used to determine other volatile substances. Flexible films made of PAni were also used to rapidly detect ammonia as a spoilage indicator in protein-rich foods with limits of detection of around 50 ppm [69]. Another conductive polymer, PEDOT:PPS, in combination with functionalized multi-wall carbon nanotubes (CNTs), was used to determine formalin in squids. In the latter, electrons are transferred to the composites when formaldehyde molecules are adsorbed on PEDOT:PSS/CNTs' surface. The hybrid PEDOT:PSS/CNTs' gas sensors act as n-type nanomaterials experiencing a carrier concentration increase upon introducing electron-donating gases. This sensor reached a LOD of 1 ppm [70].

2.2.7. Nitrates and Nitrites

Nitrates are related to diseases such as infantile methemoglobinemia, alterations in the central nervous system, and reduced motor activity. Furthermore, nitrates can be reduced in vivo to nitrites and react with amines to give rise to nitrosamines, highly carcinogenic compounds. The rise in nitrate and nitrite levels in drinking water is alarming, particularly in areas with agricultural and livestock farms. The use of inorganic and organic fertilizers in agricultural activity is the first source of contamination. However, it is also believed that manure and residues from livestock activity can contribute to the increase of the nitrates level in drinking water. Fertilizers can be a tremendous social and economic advantage, provided they are used responsibly. However, when used carelessly, the opposite effect occurs; that is, it causes an economic and environmental cost that must be assessed regarding its impact on water, climate change, ambient air quality, and waste generation [71][72]. Therefore, nitrate levels in drinking water should always be below 50 ppm. Levels between 50 and 100 ppm are acceptable but worrying, and levels above 100 ppm are hazardous [71].

For the detection of nitrates and nitrites, sensory polymers based on electrochemical responses are typically used. For example, Chu et al. developed a sensory polymer for nitrites based on three-dimensional copper nanodendrites electrodeposited on the surface of a poly(dimethyl diallyl ammonium chloride)-reduced graphene oxide modified glassy carbon electrode. The system reached a LOD of 0.06 μ M and linear response from 1 to 15,000 μ M. Similar systems have been reported based on classical PEDOT [73] but also on new polythiophene-derivative film-modified glassy carbon electrodes. The use of this new compound (2,5-di-thiophen-3-yl-thiazolo [5,4-d]thiazole) allowed the preparation of a nitrite sensor with a LOD of 2 nM, a linear response from 5.5×10^{-9} to 3.5×10^{-5} M, and excellent anti-interference ability. Another example was found using polypyronin on a pencil graphite electrode, which was tested in salami samples. The response of the sensory system was linear from 1.0×10^{-6} to 1.0×10^{-4} M, with a LOD = 5.0×10^{-7} M.

Colorimetric and fluorometric sensors have also been designed to detect nitrate and nitrite anions. Pires et al. published a study about a new fluorometric nitrite biosensor with polythienothiophene–fullerene thin-film detectors for the control of water on-site, obtaining a LOD below 0.55 μM [74]. Nitrite detection is not only intended for drinking water, despite being the most relevant issue. The amount of nitrite added in processed meats should also be controlled since it is added to show a more pinkish color and a more appetizing appearance. González-Ceballos et al. recently published a work in which an amount of nitrite in meat was detected with a polymer sensor based on four monomers, *N*-vinylpyrrolidone, methyl methacrylate, a monomer containing an aromatic $-\text{NH}_2$ group, and a monomer having an activated ring of phenol. The film-shaped polymers can change color by just contacting the material with the meat's surface, and the analysis was boosted with a smartphone app specially designed for the objective. They carried out a proof of concept with more than 15 different meat products purchased in local supermarkets [75].

2.2.8. Microorganisms

Identifying pathogenic microorganisms, mainly bacteria, in drinking water and food is relevant in key sectors of society, such as the medical field, food safety, and public health, which is why efficient and low-cost detection strategies are required [76].

In this sense, different detection systems for *E. coli*, a Gram-negative bacterium frequently found in the intestine of warm-blooded animals that can cause severe food poisoning, can be found in the literature. Yousefi et al. prepared cyclo-olefin polymer sensor films bearing epoxy functional groups. The system generates a fluorescence signal when *E. coli* is detected, and it was tested in meat and apple juice and worked at low concentrations, even at 10^3 CFU/mL [77]. This microorganism was also detected in milk samples by a surface-imprinted polyurethane–urea sensor polymer for impedimetric measurements. The system showed an LOD of 120 CFU/mL [78] in water and milk samples using a “turn on” fluorescence sensor based on an amphiphilic conjugated polythiophene [79].

S. aureus is a bacteria found in the body's microbiota in the skin and respiratory tract. However, it can become an opportunistic pathogen producing skin and respiratory diseases and food poisoning. To avoid this, Wu et al. designed an electrochemical sensor based on a dual amplification strategy of polymethylene blue nanoparticles. They tested its efficiency in human serum and food and quantitatively detected from 10 to 10^8 CFU/mL, with an LOD = 1 CFU/mL [80].

The bacteria responsible for the infection listeriosis (*L. monocytogenes*) is one of the most virulent foodborne pathogens and can produce death. Some current detection strategies include a nanoparticle cluster modified with polylysine, capable of detecting *L. monocytogenes* in the linear range of 5.4×10^3 – 10^8 CFU/mL, with an LOD of 5.4×10^3 CFU/mL [81]. Furthermore, Zhao et al. used a fluorimetric sensor based on MIPs obtained by pickering emulsion polymerization to determine the presence of bacteria (LOD = 10^3 CFU mL^{-1}) in milk and pork samples [81].

Most cases of salmonellosis are mainly caused by food (raw chicken eggs and goose eggs) infected with *S. typhimurium*. This microorganism can infect a broad range of vertebrate hosts, including cattle, sheep, horses, rodents, swine, and humans. Functionalized polymeric magnetic nanoparticles using external Raman reporter molecules (RRM) were used by Chattopadhyay et al. to detect *S. typhimurium* in spiked food products to prevent salmonellosis. The limits of detection of the bacterium were found to be 100 cells mL^{-1} and 10 cells mL^{-1} using an 4-mercapto benzoic acid (RRM1) and 5,5'-dithiobis(succinimidyl-2-nitrobenzoate) (RRM2)-based immunosensor, respectively [82]. In addition, the detection of different bacteria using the same system was possible, according to Wu et al. [70]. They used an aptasensor based on colorimetric nanoparticles modified with poly(acrylic acid). Using it, they determined *S. aureus*, *Vibrio parahemolyticus* (a bacteria that causes gastrointestinal illness in humans when ingested in undercooked seafood), and *S. typhimurium*, in aqueous solution (LOD of 25, 10, and 15 CFU mL^{-1} , respectively).

2.2.9. Other Targets

The use of sensor polymers in the detection of species, whether in the food field or any other area, is inadvertently related to dangerous or harmful targets for health. However, polymer sensors can also be used to detect targets that represent a benefit for health or enhance some of the properties of the food, such as taste, color, smell, etc. For example, quercetin is the best-known flavonoid polyphenol and is commonly used as a model for this family of organic compounds in most fruits, vegetables, and flowers. This compound has highly beneficial health properties and cardiovascular protection, including anticancer activity, anti-allergy activity, anti-ulcer properties, antiviral and antibacterial activity, and anti-inflammatory effects. Therefore, it has become a target of interest from the point of view of the quality control of specific products. Thus, Wang et al. designed a sulfur–nitrogen co-doped carbon nanoribbon (SNCNR) polymer, which can detect quercetin by forming Meisenheimer-like complexes. The mechanism of interaction of the sensory polymer and the target is by π – π stacking and electrostatic interaction, and a linear response was obtained in the range of 50.0 nM to 200 μM .

The obtained LOD was 21.13 nM [83]. Similar articles describe the development of sensory polymers for the detection of polyphenols in wines and honey [84][85], or diastase activity in honey samples [86].

Accordingly, pesticides and mycotoxins are two of the most significant targets in the wine industry. Europe is the world's largest wine producer, and these compounds are increasingly worrying producers and consumers. Pérez-Ortega et al. designed a sensory system based on solid-phase extraction (SPE) polymeric cartridges (reverse-phase sorbents), specifically two commercial brands, Bond ElutTM Plexa SPE cartridges and Oasis HLBTM SPE cartridges. The first contains a polymeric architecture with a non-retentive, hydroxylated, amide-free surface and a non-polar poly(styrene-divinyl benzene). The second includes a highly hydrophilic, water-wettable polymer with a unique hydrophilic-lipophilic balance. With this sensory system, 9 mycotoxins and 60 multiclass pesticides were studied, and LODs below 1 mg L⁻¹ for 87% of the studied compounds were obtained. In addition, the study culminates with a proof of concept with 24 red wine samples from different regions of Spain [87].

N-nitrosamines are carcinogenic compounds that can be present in food, drugs, air, water, and soil, so their control and detection is also of great importance. Lu et al. have designed metallocalix[4]arene polymers for the gravimetric determination of these compounds. *N*-nitrosodimethylamine was used as a model compound for the study, and two different polymers having calix[4]arene or 4-tert-butylcalix[4]arene tungsten-imido complexes were tested. The sensory system can detect the target in the air using gravimetric detection on a quartz crystal microbalance. The LOD of the system was 5 ppb [88].

Finally, Hu et al. have developed an ingenious method to detect acrylamide, a potentially carcinogenic substance formed in food after high processing temperatures. They first modified quantum dots with *N*-acryloxysuccinimide. Afterward, the polymerization of acrylamide occurs, and this novel fluorescence detection method relies on the distance increment between quantum dots induced by the polymerization. The system has a linear range of 3.5×10^{-5} to 3.5 g L⁻¹ and an LOD of 3.5×10^{-5} g L⁻¹, and the methodology was tested with potato chips [89].

2.3. Water and Beverage Treatment. Extraction (Elimination) of Target Species

2.3.1. Desalination

The desalination of seawater is usually performed using aromatic PA-based membranes. However, they present some challenges, such as fouling or low permeability. Recently, various approaches have been addressed within this framework to improve the properties of this type of PA-based membranes.

The fabrication of new hybrid organic-inorganic materials through the integration of nanoparticles in polymeric matrices has offered a new strategy for preparing membranes with higher permeability, high selectivity, and better antifouling characteristics. Bano et al. prepared integrated PA nanofiltration (NF) membranes with different graphene oxide (GO) contents. The flux of the new membranes was 12 times higher than in its 100% organic version, and the antifouling properties of the membrane were significantly improved due to an increase in hydrophilicity. These properties were evaluated against bovine serum albumin and humic acid [90]. Similar studies were carried out in which a thin-film composite nanofiltration membrane was prepared with a wrinkled polyamide layer, prepared by interfacial polymerization on a support composed of carbon nanotubes/polyether sulfone [91]. The membrane presented a permeability of up to 53.5 L m⁻² h⁻¹ bar⁻¹ with a rejection greater than 95% for Na₂SO₄.

Another alternative to traditional PA membranes are the Turing-type membranes. Turing structures appear when imbalances in diffusion rates make a stable steady-state system sensitive to minor heterogeneous perturbations. Tan et al. prepared Turing-type PA membranes by interfacial polymerization and obtained membranes with à la carte shapes, such as bubbled or tube structures. Water transport through membranes and their performance is excellent and promising. Some authors have reported excellent results using polymers different from PAs for water desalination, such as poly(2-(diethylamino)ethyl methacrylate) and poly(2-(dimethylamino) ethyl methacrylate). The microgels showed a water flow of 56 L·m⁻²·h⁻¹ and a water recovery of 50% [92]. In another example, Lu et al. developed a methodology for adjusting the permselectivity of cellulose triacetate membranes by a swelling and deswelling procedure induced by plasticizers added to the formulation of the membranes. Membranes demonstrated a decrease in water and salt permeability due to reduced crystallite size in the crystalline regions and chain mobility in the amorphous regions. Since the salt permeability was higher than water, the result was a higher permselectivity and an improved desalination performance. The development allows the design of polymeric membranes with properties of interest in the field of desalination [93].

Zhang et al. have found an ingenious way of applying polymer science and technology in the desalination of seawater. In this case, the technique was capacitive deionization, an emerging eco-friendly technology with high energy efficiency and

low operating cost ^{[94][95]}. Their study focuses on electrode cleanliness, precisely electrode antifouling properties, which are enhanced when a poly(sulfobetaine methacrylate) brush coating is prepared by surface-initiated atomic transfer radical polymerization. These brushes clean the electrode and prevent dirt from embedding in them for at least 100 desalination/regeneration cycles ^[96].

In addition to nanofiltration membranes, there are other methods for water desalination. Solar desalination is a sustainable method with a great future, but it requires high-rate solar evaporation, which is generally difficult to achieve, and the process is inefficient. Zhou et al. have designed a polyhydrogel that works as a solar evaporator able to generate steam at $\sim 2.5 \text{ kg m}^{-2} \text{ h}^{-1}$ under solar irradiation of 1 kW m^{-2} . The hydrogel is based on EVOH and reduced graphene oxide. The former diminishes the enthalpy of water evaporation, and the latter is a solar absorber that improves efficiency. In addition, this hybrid material contains internal capillary channels that allow continuous steam generation and excellent antifouling properties, resulting in an efficiency of about 95% ^[97].

2.3.2. Toxic Metals

Some heavy metals (such as arsenic, lead, mercury, and cadmium) are included in the World Health Organization's list of Chemicals of Major Public Health Concern ^[98], and they can be found in tap water. Therefore, their extensive use causes environmental contamination, and, in addition, they are cumulative toxicants that affect multiple body systems, including gastrointestinal, cardiovascular, renal, neurologic, and hematologic systems. Consequently, the interest in eliminating heavy metals from drinking water produces countless publications yearly. This number was multiplied by six in the last decade, with reported methods based on adsorption; membrane; and chemical, electric, and catalytic treatments.

2.3.3. Denitrification

Nitrates can end up in drinking water mainly because of their extensive use in fertilizers, manure, and liquid waste discharge from septic tanks carried by rain or irrigation. The denitrification process (removal of nitrates from water) is complex. Despite the many techniques that can be used, three of them are the most relevant from a polymer science point of view, namely, the use of bioreactors, adsorptive membranes, and ion-exchange materials.

Chu et al. designed a fixed bed bioreactor loaded with a PCL biopolymer, which acts as a carbon source and biofilm carrier. During the study, the average NO_3^- in the effluent was less than 3.7 mg N L^{-1} , and more than 95% of total nitrogen was withdrawn at a hydraulic retention time of 3–6 h ^[99]. The same authors carried out similar studies by using three kinds of biopolymers blends (poly-3-hydroxybutyrate-co-hydroxyvalerate (PHBV), PHBV/starch, and PHBV/bamboo powder) as carbon source and biofilm carriers, obtaining removal efficiencies of about 90% ^[100].

Regarding ion-exchange materials, Nabid et al. found a new use for conducting polymers as stable nanocomposites for nitrate ion exchange materials ^[101]. The nanocomposites were made of multi-walled carbon nanotubes with different polymers (poly(1,8-diaminonaphthalene), polypyrrole, PANi, and poly(2-vinylpyridine)). This way, removal efficiencies around 1.20 g L^{-1} were reached at $\text{pH} = 6.5$ and ambient temperature. In other relevant publications, different polymers were used with the same aim as cellulose nanocrystals (CNC)-grafted copolymers of 2-(dimethylamino)ethyl methacrylate and coumarin monomers ^[102], PS modified with amino and quaternary ammonium groups ^[103], chitosan/PEG and chitosan/PVA polymer composites ^[104], and polyacrylonitrile–alumina nanoparticle mixed-matrix hollow-fiber membranes ^[105].

2.3.4. Fluoride Elimination

Fluoride is present in natural rocks (sellaite, cryolite, fluorapatite, etc.), but the high levels found in water are directly caused by human actions, such as the excessive use of phosphate fertilizers. The International Organization for Standardization proposes acceptable fluoride values in drinking water from 0.5 to 1.0 mg L^{-1} . However, many Asian countries show 35 times higher concentration values in drinking water, which is alarming. Moreover, both excess and deficiency of fluoride can lead to health problems, such as dental caries or skeletal fluorosis, respectively ^[106].

Consequently, diverse technologies have been developed to reduce the fluoride amounts in water, such as coagulation, adsorption, precipitation, and membrane separations. However, pressure-driven polymeric membranes made of PAs, polyvinylidene fluoride, polyurethane, polyacrylonitrile, and polysulfone are the most relevant technologies from a polymer-science viewpoint ^[106].

2.4. Polymers for the Separation of Targets

MIPs are probably the most relevant family for solid-phase extraction (SPE), solid-phase microextraction, dispersive SPE, stir bar sorptive extraction, magnetic separation technology, etc. Applied to food technology, there are some relevant

publications in the last decade, as published by Jiang et al. They reported the separation and determination of carbohydrates in food samples (milk, honey, juice, candied jujube, beer, and chitosan oligosaccharide capsule). Under the most favorable conditions, 32 carbohydrates, including mono, di, and oligosaccharides and sugar alcohols, were separated in less than 12 min. The technique carried out was capillary electrophoresis, but the key was the use of a cationic polymer of hexadimethrine bromide as an electroosmotic flow reverser ^[107].

Another MIP-based publication was reported by Wang et al. for the separation of glibenclamide in health foods, a drug for treating type 2 diabetes. The MIPs were prepared using dendritic-grafting magnetic nanoparticles, with methacrylic acid (functional monomer) and with a cross-linker (glycol dimethacrylate), rendering the recovery of glibenclamide in spiked health foods of 81.46–93.53%, with an RSD < 4.07% ^[108]. Similar works have been published for the separation of zanthoxylum alkylamides from prickly ash powder ^[109]; sunset yellow (E110) from fruit juice, fruit juice powder, and pharmaceutical samples ^[110]; dichlorodiphenyltrichloroethane ^[111] and cadmium ^[112] from various food samples; mercury(II) ions from fish samples ^[113]; lead from aqueous samples ^[114]; or citrinin from maize ^[115].

However, in recent years, promising competitors have emerged for MIPs, such as open-tubular capillary electrochromatography (OT-CEC) using grafted polymers. Specifically, two publications stand out in the literature, in which Aydoğ̃an et al. describe the preparation of open tubular columns by the in-situ grafting polymerization of 3-chloro-2-hydroxypropyl methacrylate (HPMA-Cl) for the separation of malic acid amino and acids enantiomers ^{[116][117]}. In the first case, the polymerization of HPMA-Cl is followed by a modification with L-histidine and in the second case with β -cyclodextrin (β -CD).

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