Ashutosh Kumar Shukla *Editor*

Food Packaging: The Smarter Way

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To my parents.

Preface

Food packaging is of interest to different stakeholders including producers, retailers and consumers in view of societal and environmental concerns. Right choice of packaging materials to improve packaging experience and shelf-life are therefore the areas that have attracted the scientific community. This volume is a collection of different chapters dealing with novel packaging materials and trends from pre- to post-packaging of food items. Initial chapters have been planned to acquaint the audience with food packaging industry and provide a link to latest research on smarter ways of food packaging including artificial intelligence applications. Biodegradable packaging solutions for fruits, vegetables and animal-based food products including dairy and fishery products have been covered in the following chapters. Edible films and coatings have been presented in a separate chapter highlighting the challenges and applications. Role of sensors to improve food packaging has also been presented in a separate chapter as well. Similarly, another chapter presents the applications of functional nanomaterials for food packaging. Rules and regulations related to the packaging have also been included to bring in the sense of completeness.

While going through the chapters, I learnt many things and expect the same for the intended audience including novice researchers. I thank the expert contributors from different laboratories/countries/disciplines making this volume truly interdisciplinary. Some of the authors accepted my request to review the individual chapters and provided their valuable comments. This helped me a lot to present the quality content before the readers.

I sincerely thank Dr. Naren Aggarwal, Editorial Director—Books, Asia, Medicine & Life Sciences, Springer for giving me the opportunity to present this book to the readers. I also thank Madhurima Kahali, Editor Books—Medicine & Life Sciences, Springer and Mr. Suraj Kumar, Production Editor (Books), Springer for their support during different stages of publication.

Prayagraj, Uttar Pradesh, India
Ashutosh Kumar Shukla

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Food Packaging Industry: An Introduction

1

Vilásia Guimarães Martins and Viviane Patrícia Romani

1.1 Introduction

The basic materials used in the food packaging industry are glass, metal, paper and paperboard, plastics, or their combinations in the same material. Innovations in the sector of food packaging are adding many different compounds and using various technologies to produce intelligent, active, sustainable, and biodegradable packaging.

There is a growing demand from consumers who desire safer, high-quality, extended shelf life, and less processed food products. In this case, the innovations in terms of packaging are remarkably interesting. Active compounds with antimicrobial and antioxidant properties, for example, can be incorporated in the packaging material. These compounds are released throughout the product's shelf life, and then, it is not necessary to add preservatives in the food product formulation. This type of material is called active packaging. Another technology highlighted in recent years is the intelligent packaging, which also contributes for food safety. Intelligent packaging informs the consumer through indicators and/or labels if the food product is appropriated to be consumed, even if it is within the expiration date described on the product packaging. In some cases, food products are not stored, transported, or even handled at the appropriate temperature, reducing their shelf life. Through intelligent packaging, consumers will know if the product was appropriately transported and handled, and thus, they will be sure about the quality of the product.

The world produces about 300 million tons of plastic waste each year, and so far, only 9% of this waste has been recycled (ONU 2019a). Also, each year at least eight

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million tons of plastic go to sea and oceans, often decomposing into small microplastics that end up in our food chain (ONU 2019b). Durability, resistance, lightness, flexibility, and low cost are some of the characteristics that make the plastic unique and indispensable in daily life (Heidbreder et al. 2019). However, the qualities that make the plastic a good material for consumer products can also make it extremely resistant to biodegradation and can remain in the environment for decades.

Given the above, a sector of the packaging industry that is expanding is the sustainable and biodegradable packaging. Research has been carried out all over the world trying to find solutions to make possible to replace mainly the synthetic plastic packaging by biodegradable packaging. The main raw materials used to produce biodegradable packaging are proteins, lipids, and carbohydrates, usually extracted from agroindustrial sources, and waste from food industries. Important findings are reported in the production of biodegradable materials for food packaging; however, their use is still limited due to the mechanical and barrier properties, which are inferior to those of synthetic polymers. Several techniques have been used by researchers to improve these properties, including the use of blends, chemical modifications of polymers, addition of reinforcement materials (e.g., nanoparticles and fibers), application of plasma, and UV light treatments.

In addition to the sustainable, renewable, and biodegradable materials being used in the development of new plastic packaging, it is also possible to observe this environmental concern for other materials as well. For example, the immense exchange that is taking place from glass, metal, and plastic packaging by cellulosic packaging also has this environmental appeal. Today is possible to find whiskey “bottles” in cardboard on the market, which would have been unthinkable a few years ago.

This chapter will briefly discuss information about the global food packaging market, innovations in the food packaging sector, and what are the challenges and perspectives for the packaging produced in research laboratories to reach the market.

1.2 Global Food Packaging Market and Sustainability

According to the World Packaging Organization (2020), the revenue of the global packaging industry is over USD 500 billion. Sustainability, convenience, efficiency, protection, and flexibility are the parameters associated with packaging solutions. For consumers, easy-to-use and sustainable packaging is becoming a priority now than ever before.

There are a lot of market analysis reports about the global food packaging market size at the Internet. Most of them project the future market of food packaging based on type of material, application, outlook, region, among others. The growth of the food packaging market is estimated based on some factors such as convenience, increase in the population, improvement of the shelf life, single serve packs, food delivery, and high-performance materials; all these parameters have a positive impact on the market. In the industries, the consumers’ desire is what drives the vector of changes, and in the packaging industry, it would be no different. In addition to the improvement of the consumer experience when unpacking a product, its design and how it relates to sustainability also matter.

About 40% of all plastic produced in the world is used for food packaging, followed by building and construction industry (20%) (PlasticsEurope and EuPR 2015). Governments have been acting to reduce environmental impacts, establishing agreements with brands to reduce or change the use of raw materials, such as plastic. In the United Kingdom, for example, the government will introduce a tax on plastic packaging from 2022. Besides that, financial sanctions will be established to encourage the incorporation of recycled plastic in the production chain of these companies, creating an interesting precedent for their adhesion.

As mentioned by the Grand View Research (2020), the paper and paper-based material segment accounted for a revenue share of 31.9% of the total food packaging market in 2019. Growth of this segment is driven by high product adoption to substitute nonbiodegradable packing solutions. Innovations in design, ease of printability, and sustainability give paper packaging a competitive advantage over plastic and metal packaging solutions.

Regarding bioplastics, which represents a crucial way to reduce the environmental burden, European Bioplastics, Nova-Institute (2020), mentioned that the global production capacities of bioplastics including bio-based and biodegradable materials are 2.11 million tons in 2020. Bio-based/nonbiodegradable materials (PE, PET, PA, PP, PTT, and other) represent 41.9% of the bioplastics produced, and biodegradable materials (PBAT, PBS, PLA, PHA, starch blends, and other) represent 58.1% of the total. Going forward, the conscious consumption will be the meeting point for transformations in the global food industry. Implementing sustainable policies and philosophies in the manufacturing lines, from the product itself, through packaging and logistics, will be a necessity to survive in a modern market that is concerned with the planet.

1.3 Sustainable Food Packaging

Plastics are the most used materials in packaging applications in different fields. Commonly used polymers, such as polyvinylchloride (PVC), polyethylene terephthalate (PET), polypropylene (PP), polyethylene (PE), polyamide (PA), polystyrene (PS), and ethylene vinyl alcohol (EVOH), are cost-effective and have enough properties to protect packaged products since production to consumption (Geyer et al. 2017; Luzi et al. 2019). However, these fossil-based polymers are obtained from finite sources. In addition, the incorrect plastic disposal, which has a nonrecyclable or nonbiodegradable nature, is driving the growing need of sustainable alternatives, due to the environmental burden resulting from the high amount discarded (Ahmed et al. 2018).

Sustainable materials protect the environment since the raw material extraction to the final disposal, meaning that there is no damage to the nature. The food industry is one of the largest users of packaging (All4Pack 2018) and thus has a valuable responsibility in using sustainable packaging as well as motivating industries and consumers to adhere to the use of such materials. Then, the idea is to use renewable and abundant resources to produce biodegradable/compostable alternatives. In this context, it is important to consider that plastics produced by renewable resources are not certainly biodegradable or compostable. Likewise, biodegradable materials are not necessarily produced with renewable resources, as biodegradation is related to the chemical structure in the matrix instead of its origin (Lambert and Wagner 2017; Asgher et al. 2020). In summary, a sustainable packaging is a material obtained from renewable sources that in the end of its cycle is biodegraded or composted.

Bioplastics are a potential alternative that can contribute to the sustainable development in food packaging. Biopolymers or natural polymers can be generated by plants or microorganisms and/or extracted from food industry by-products. Some examples include carbohydrates (e.g., chitosan, starch, cellulose), proteins (e.g., keratin, gluten, collagen), polylactic acid (PLA) polyhydroxyalkanoates (PHAs), and exopolysaccharides (EPSs) (Benbettaïeb et al. 2016; Asgher et al. 2020), which are being widely explored in the development of films, wraps, and laminates for food packaging. Some examples of recent developments include an edible film packaging made from a milk protein for dairy, a box for pasta packaging prepared with wasted vegetables and fruits, and a plant-based paper cup (TrendHunter 2017).

The production of bio-based materials for food packaging is a multistep process. Generally, it starts with the breakage of the intermolecular linkages of the biopolymer, followed by the synthesis of a new molecular structure and finally the development of the three-dimensional network from the new linkages formed (Galić et al. 2011). The resulting material characteristics depend on the raw polymer structure and the processing conditions. Bioplastics can be produced by wet or dry processing (Blanco-Pascual et al. 2013). Wet processing, known as casting technique or continuous spreading, is based on the solubilization of the biopolymer in the solvent with the posterior solvent evaporation. The final polymer is influenced by the pH and temperature of the suspension, and the type of solvent (Khwaldia et al. 2004; Mellinas et al. 2016). Differently, the dry processing, including extrusion, or thermal processing, depends on the thermoplastic properties of the polymers, based on the theory of glass transition. This method consists of the conversion of the glassy structure into a semi-solid condition at a specific temperature, where the molecules are broken, and new linkages and bonds are formed (Khwaldia et al. 2004; Hernandez-Izquierdo and Krochta 2008).

Bioplastics can also be incorporated with various additives, for example, antioxidant and antimicrobial compounds, nutrients, and colorants. Agricultural by-products are a potential and cheap source of renewable additives. These additives reduce the possibility of microbial growth and lipid oxidation, and also have the capacity to increase the shelf life of products (Jafarzadeh et al. 2020). Studies reported the incorporation of various additives from renewable sources in different matrices, such as durian leaf waste to enhance antioxidant activity in gelatin films (Joanne Kam et al. 2018), jambolão skin extract in methylcellulose films to provide antioxidant and color-changing properties (da Silva Filipini et al. 2020), grape seed extract—carvacrol microcapsules in chitosan films to increase the shelf life of refrigerated Salmon (antimicrobial properties) (Alves et al. 2018), chitosan nanoparticles in starch films to inhibit bacteria in wrapped cherry tomatoes (Shapi'i et al. 2020), pomegranate peel particles into starch-based films as antimicrobial and reinforcing agent (Ali et al. 2019), kombucha tea in chitosan films to retard lipid oxidation and microbial growth in minced beef (Ashrafi et al. 2018), and pink pepper phenolic compound incorporation in starch/protein blends to inhibit apple browning (Romani et al. 2018). Bioplastics have strong potential as sustainable alternatives to synthetic materials because they are produced using renewable sources, a prerequisite as previously mentioned, and despite some challenges that their use still faces (discussed in the section ahead), generally they present fast biodegradation in soil and water.

1.4 Technology Developed in the Laboratories X Scale Up to Industries

Sustainable materials have been broadly studied and interesting results are being obtained, but the large-scale production for commercial uses is still limited and the commercial use is insignificant compared to the conventional plastics. There are different reasons that prevent the wide use of sustainable packaging, including (1) the material properties, which are not enough to protect the products and can compromise the food shelf life; (2) scale-up, since the process of production, development of the new technology, and financial capacity; (3) production and logistic for feedstocks and composting infrastructure; (4) regulation policies; and (5) consumer behavior (Rydz et al. 2018; Steenis et al. 2018; de la Caba et al. 2019).

New sustainable materials for packaging are generally produced using hydrophilic biopolymers, which result in the low physicochemical properties (such as mechanical and barrier performance) due to sensitivity to humidity. To overcome these limitations, researchers are searching for strategies for material improvement. Examples of strategies are the incorporation of reinforcing agents, blending different raw materials, and chemical, enzymatic, and physical methods to alter polymer chains (Bourtoom 2009). Promising results are being obtained; however, the challenge is the improvement of the overall performance of the polymer. Usually, the increase in the mechanical resistance does not come with the increase in barrier properties and vice versa. Indeed, the protection of foods requires the equilibrium of different material's characteristics to prevent the component oxidation and microbial spoilage, and thus, attention is necessary at the minimum performance necessary in the packaging to keep the quality of products (Martins et al. 2019). Additionally, the change in the properties of bioplastics during the interaction with the food material needs to be considered. Either, the compatibility of the polymers with the products can affect the food quality and gained minimal attention (Asgher et al. 2020).

Another important hurdle that affects the wide adoption of biopolymers use is the difficult scale-up of the production process. The production of biopolymers in laboratories is widely performed through the casting technique. It consists of pouring a suspension on plates (e.g., Petri dishes) controlling the mass of suspension to generate an uniform thickness, but variations are difficult to avoid. This technique is suitable to produce films up to 30 cm, not larger, and takes long time in the drying step making it useless at industrial scale. The tape casting, which consists of the spreading of suspension in larger supports or on continuous carrier tapes, is useful to produce larger films, but industries in general have well-established extrusion processes (De Moraes et al. 2013; Werner et al. 2017). To advance in the large-scale production of biopolymers, the proof of concept needs to be effectively produced in industries. Even though some biopolymers are not suitable for extrusion processes, as in the case of proteins due to their molecular architecture and spatial arrangement (Mensitieri et al. 2011), it is important to focus on strategies to adequate such polymers in a way to facilitate their processing by the industry technologies. Generally, industries adopt and license unique raw materials to produce plastics, and then, an industry adjustment would be necessary for the production of the biopolymers. In addition, besides the fact that academic research mostly stops at the proof-of-concept stage, patented technologies are frequently incomplete in scope to be adopted by industry (Nerkar and Shane 2007; Tolfree and Jackson 2008; Inns 2012), impeding the advance of such technologies. That is why, it is also important the pilot scale fabrication and characterization, otherwise it is possible to be financially inviable for industries to take high risks to adopt the sustainable technologies for packaging (Werner et al. 2017).

1.5 Final Remarks

To increase the use of biopolymers, besides the mentioned aspects, the resource efficiency and composting infrastructure need to be considered, as well as the regulation policies. Currently, raw materials used to produce biopolymers often compete with requirements for food-based products. The expansion of the first-generation bio-based polymer production can generate unsustainable demands (Babu et al. 2013). Furthermore, a composition structure is necessary for the suitable biopolymer disposal. As the definition of ASTM-D6400, a compostable material is a material that biologically degrades; therefore, just substances that can degrade biologically in a composting environment can be labeled as “compostable” (ASTM D 2004). In this sense, besides the processing of biopolymers, it is fundamental to the planning of resource efficiency, raw materials obtaining, and composting infrastructure in the end of the biopolymer life.

Also, the consumer purchase probability and willingness to pay for sustainable materials have a critical influence in the advance of new biopolymer technologies. The consumer acceptance of these new materials has also an important role. Firstly, the higher costs of biopolymer production result in superior market prices and consumers usually do not pay the price for sustainability. Also, traditional consumers can question the quality and/or safety of the new material due to the limited information about the advantages and the low familiarity with biopolymers (De Marchi et al. 2020). In addition, consumer insights related to sustainable designs help designers to develop coherent strategies to adopt new initiatives. The lack of these consumer insights also complicate the adoption of new sustainable alternatives (Steenis et al. 2018). Still regarding the attitudes to adopt sustainable materials, industries have an essential role as well. Some manufacturers tend to support the use of old technologies and prevent the adoption of more sustainable solutions due to the efforts needed in adjusting their processes (Keränen et al. 2020). Therefore, reorientation of existing industries toward sustainability demands more attention and consumers need to be informed regarding the importance of sustainable packaging and motivated to consume such products.

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World Packaging Organization (2020)

2 Toward Smarter Food Packaging

Bambang Kuswandi

Abstract

Many food producers regularly know about new food packaging options, i.e., smart packaging, active packaging, intelligent packaging, and connected packaging. This chapter review shows that these types of packaging benefit specific types of food products, so producers can decide which ones most help them. Smart packaging is an umbrella term used to describe food packaging with enhanced functionality through technology. However, intelligent packaging that will be focused on in this chapter contains sensors to determine the condition (e.g., freshness or ripeness) of the food products. Another term used in smart packaging is active packaging, where it is used to interact with the packaged foods to enhance their condition, significantly to extend freshness or shelf life. In comparison, connected packaging allows consumers to interact with a food product through a label or code on the package that can be activated with a mobile device. Finally, the role of I.T. in smart packaging applications for food quality and safety monitoring is discussed.

Keywords

Smart packaging · Intelligent packaging · Sensors · Perishable foods · I.T

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2.1 Introduction

There will be many food products that lose their nutritional values and properties fastly if they are not packaging properly. Food packaging plays a very important role in the food supply chain management system. Since it can be employed as a protective layer to avoid food contamination and maintain food quality and safety (Bambang Kuswandi et al. 2011), however, the classical food packaging system can only protect or isolate food product from the external condition and environment without informing food quality, such as freshness and safety, for users (Kuswandi and Moradi 2019). Physical, chemical, and microbial properties and sensory evaluation are traditional methods for the determination of food quality and safety. The drawbacks of these methods are laborious works, long procedure, high cost, requiring sample pretreatment, and destructions. Based on these methods, the detection of food quality and safety is difficult to be performed in fast and nondestructive methods. Therefore, smart food packaging that informs the consumer regarding the food quality and safety evaluation is needed. It drives by the recent trends and consumer needs as well as regulatory requirements on food products.

Food packaging also plays a crucial role in reducing waste and carbon dioxide (CO_2) caused by used packaging and their disposal (Kuswandi 2017). This is due to the fact that our society has produced 8.3 billion metric tons of waste, where it contains 76% of plastic, which is mainly not recycled (90.5%) for over the last 60 years (UN Environment Programme 2018). Furthermore, the current situation due to the pandemic of COVID-19 caused food scarcity, which has to pay further attention to the food waste problem. Even though all in the food sectors have a role play in avoiding and decreasing food waste, starting from food producers to consumers, the significance of domestic waste recommended that innovative packaging can be an important tool for preventing and reducing food waste. In this regard, packaging has become an important technology to assure quality and safety in the food supply chain, enhance shelf life of foods, fulfill consumer satisfaction, and prevent undesired consumer complaints (Kuswandi 2020). Since consumers are more concerned about food quality and safety and require more accurate food information on quality and safety, in this case, it needs to provide a simple and real-time monitoring method for food product quality and safety during food supply, distribution, storage, and display according to the consumer interests and rights. Although there are many major innovations in food packaging systems and materials, the basic food packaging principles are still the same. Among them, smart packaging systems offer a great approach in reducing or even preventing food wastes.

Smart packaging, especially intelligent, active, and connected packaging, could support the optimization of the food supply management system, such as enhancing food shelf life and food quality monitoring, and reducing food loss and waste. Active packaging system helps in increasing the food product shelf life, enhancing their condition, and significantly extending food quality by “interacting” with the food product, while an intelligent packaging system helps in informing the food product quality and safety during transportation and storage as well as a display by “monitoring” the food product condition (Kuswandi et al. 2011; Kuswandi 2017; Rai et al. 2019). Furthermore, the connected packaging allows consumers to interact with a food product via package label or code that can be accessed using a mobile device. This chapter discussed smart packaging that will be more focused on intelligent packaging development over active packaging since its “monitoring” function could enhance to be smarter with the help of ICT via Apps, artificial intelligence, or IoT (Internet of Things). In this case, connected packaging concepts are also discussed that allow consumers to interact with a food product through a label or code on the package that can be activated with a mobile device.

2.2 Intelligent Packaging

Based on the Commission of the European Communities, it is stated that intelligent food contact materials are defined as materials that allow monitoring the packaged food condition or the environment surrounding the food (Communities 2004). Hence, intelligent food packaging could be defined as a new packaging technology that integrates intelligent functions with food packaging systems. Intelligent packaging can detect, sense, trace, record, and communicate internal or external changes related to food products that associate with the formation of food quality and safety, and extended the packaging information functions during transport, storage, and display that promotes and enhances safety and quality of food producers or consumer (Kuswandi et al. 2011; Salinas et al. 2014a, b). The intelligent packaging functions are given in Fig. 2.1. Intelligent packaging performs the communication functions on the packaged food condition during distribution, storage, sales, and packaging waste disposal to food producers and consumers (Yam et al. 2005).

In order to allow real-time or online monitoring of a food product during distribution, storage, and display, numerous smart devices are employed, such as indicators (for monitoring food freshness, pH, leakage, integrity, time, and temperature), data carriers (bar codes, IoT), and sensors (gas chemical sensors and biosensor) (Ghaani et al. 2016; Kuswandi 2018; Müller and Schmid 2019). Intelligent packaging allows many applications in food freshness detection, spoilage, chemical, and microbial contaminant detection, traceability, authentication, etc. (Majid et al. 2018; Kalpana et al. 2019; Vanderroost et al. 2014; Popa et al. 2019). Some current example of various smart devices used and integrated into intelligent food packaging is shown in Table 2.1.

2.2.1 Freshness Indicator

A freshness indicator is a smart colorimetric device integrated into intelligent food packaging. This type of colorimetric indicator is divided into two types: direct colorimetric indicator and indirect colorimetric indicator as given in Fig. 2.2 (Kuswandi et al. 2011). The direct colorimetric indicator commonly works based on color development of indicator caused by the volatile gas released by food that

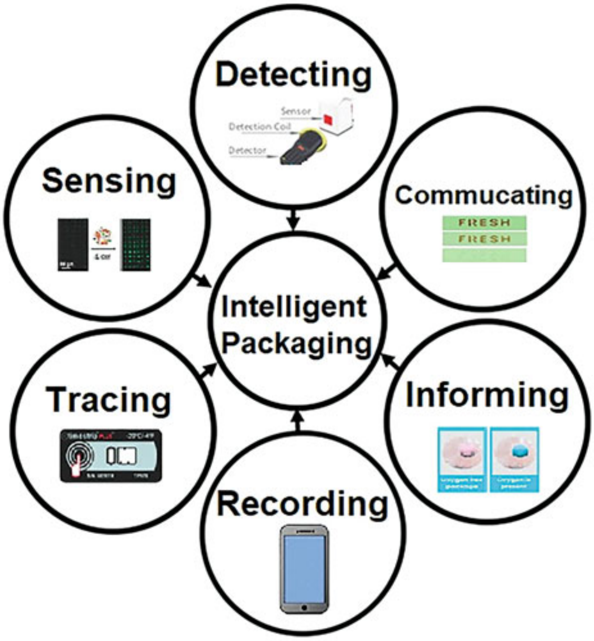

Fig. 2.1 Intelligent packaging functions in food packaging

Table 2.1 Some current examples of various smart devices integrated into intelligent food packaging

Type of smart device	Sensitive material	Target analyte	Material used	Type of food	References
Indicators	Black carrot	pH	Bacterial cellulose	Pasteurized milk	Ebrahimi Tirtashi et al. (2019)
	Red cabbage	pH	Bacterial cellulose	Pasteurized milk	Kuswandi et al. (2020)
	Alizarin	pH	Chitosan	Fish	Ezati and Rhim (2020)
	Shikonin	pH	CMC CNF	Fish fillet (mackerel)	Ezati et al. (2021)
Gas sensor	Oxygen sensor	O_2	A blending of polyethylene and ethylene-vinyl acetate	Beef	Kelly et al. (2020)
	RFID	O_2 and CO_2	Wheat gluten	Cheese	Saggin et al. (2019)
	RFID	O_2 and CO_2	Cellulose	Vegetables	Eom et al. (2012)

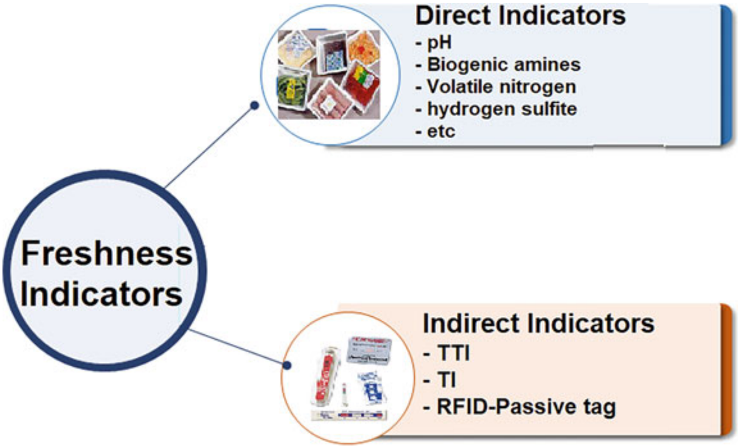

Fig. 2.2 Types of freshness indicators

can be directly related to the food freshness. This colorimetric indicator allows for qualitative or semi-quantitative detection of food quality and safety as a result of physiological changes or microbial growth during food storage, which directly integrated into food packaging, where it can help consumers to judge food quality easily by the naked eye (Ghaani et al. 2016; Kuswandi 2018), while indirect colorimetric indicator works based on imitating or mimicking degradation of targeted food to be monitored, for example, TTI (time–temperature indicator) and T.I. (temperature indicator) (Kuswandi 2018; Kuswandi 2020). In other perspectives, these freshness indicators could also be classified into two types, i.e., the first one is an internal indicator, and the second, external indicator. The internal freshness indicators are placed inside the food package, and the external freshness indicators are physically placed outside the food package (Pavelková 2013). Both types of freshness indicators can inform consumers related to the presence or absence of specific compounds, or the concentration of a specific substance, related to the level of food freshness. Thus, a distinct characteristic of freshness indicator is the type of information they provide, either qualitative or semi-quantitative toward the user for freshness level.

Freshness indicators employed in food packaging inform a consumer on the issue of food quality and safety related to food degradation due to microbial activity or other food properties. Mostly, the information is presented by immediate color change variations, such as different color intensities or the dye diffusion inside the indicator area (Kalpana et al. 2019; Kuswandi 2020). Even though freshness indicators are simple devices but crucial in assuring food quality and safety, they allow a reduction in the food loss and the cost loss due to the food damage. Therefore, it is very useful for nondestructive testing of food freshness, especially for perishable foods and dairy products, such as fish, meat, milk, fruits, and vegetables. Therefore, in other senses, it is also called a spoilage indicator since it is also used to indicate food deterioration or spoilage. Even though intelligent food packaging has many benefits for perishable foods, however, its application in the food industry is still limited, and it needs further exploration and commercialization.

Commonly, freshness indicators are monitoring the packaged food quality by detecting metabolite compounds produced associated with the food freshness causing by natural metabolism or microbial growth (Kuswandi et al. 2011; Realini and Marcos 2014). Physicochemical changes during food distribution and storage are indicators for food freshness. Food metabolites change during storage, such as pH, lactic acid, carbon dioxide, ethanol, volatile nitrogen, biogenic amines, or hydrogen sulfite, are an indication of microbial activities inside foods, which, in turn, can be employed as indicators of food freshness (Arvanitoyannis and Stratakos 2012; Kuswandi et al. 2011). Freshness indicator monitors food freshness via this metabolite detection that has been reported in the literature (Kuswandi 2018), even though, their successful commercialization is still limited. For instance, FreshTag® and Toxin Guard™ are commercial freshness indicators that have been discontinued. The former was a colorimetric freshness indicator that detects the volatile amines produced in fish, based on the immobilization of antibodies into plastic films to detect food pathogens (Kuswandi et al. 2011).

2.2.2 Ripeness Indicators

Freshness indicators are mainly employed for freshness monitoring of protein-based food products, e.g., meat and seafood. Besides these, particularly, fruits and vegetables produce a large number of volatile compounds during ripeness and maturation that can be used to indicate ripeness and maturity. For the first time, in 2004, P-P Enterprise's supermarket in New Zealand released a new ripeness indicator, namely ripeSence (T.M.) for pear, as a new intelligent packaging system. It is the first intelligent label in the world that can indicate the fruit ripeness or maturity or even rotten. The ripeness indicator could detect fruit ripeness by determining the fruit aroma compounds released during fruit ripening. Volatile aldehydes, such as acetaldehyde produced during stone fruit maturation, such as apple, could be used to detect their maturity. An indicator label based on methyl red can detect the release of aldehyde from an apple. The ripeness indicator is fabricated by special ink printed directly on a paper medium. Under mature conditions, the indicator color developed from yellow to orange and then to red (Kim et al. 2018).

Ethylene produce can directly relate to fruit ripeness or vegetable maturity. A colorimetric ripeness indicator for color change upon reaction with ethylene has been developed. The indicator can be used to indicate the ripeness or maturity via the ethylene release during ripening of fruits and vegetables, such as apple (Lang and Hübert 2012) and kiwifruit (Hu et al. 2016). With the development of ripeness indicators, a variety release of aromatic substances during fruit and vegetable maturation or rotten can be employed as releases indicating fruit and vegetable ripeness.

pH could also be used as an indicator for fruit freshness since many metabolite changes during fruit ripeness or vegetable maturity relate to the pH change inside

Fig. 2.3 Ripeness indicators were used for monitoring fruit ripeness (freshness) for strawberries (**a**) and grapes (**b**)

food packaging (Kuswandi 2018). For example, a ripeness indicator was developed for monitoring guava (*Psidium guajava* L.) freshness based on immobilized bromophenol blue onto a cellulose membrane by absorption (Kuswandi et al. 2013). The ripeness color indicator developed from blue to green as the pH declined as a result of the guava over-ripening, where at this stage, the volatile organic compounds were released. This indicator was successfully applied to detect the guava ripeness at ambient temperature (28–30 °C). Furthermore, fruit ripeness indicators have been developed by the same group for strawberries (Kuswandi 2013) and grape (Kuswandi and Murdyaningsih 2017) using a similar principle based on pH change in fruits monitored as given in Fig. 2.3. Another indicator for vegetable maturity was developed based on a silver nanoparticle that has yellow color as a colorimetric sensor for the detection of organosulfur compounds produced when onion spoilage. The color developments were observed during 10 days, where the color developed with time, from yellow to orange, then pink, and lastly colorless when the onion spoilage.

2.2.3 Other Indicators and Sensors

Other indicators or often called colorimetric sensors since these smart devices can be classified as colorimetric chemical sensors or biosensors depend on the sensitive membrane or film used. One example of this type of indicator is integrity indicator, where it is informing regarding how long a packaged food has been opened or inform the gases presence inside the food package. Usually, this integrity indicator is employed with MAP (modified atmospheres in packaging), where the oxygen gas replaces other gases, such as nitrogen or carbon dioxide, which, in turn, enhances the shelf life of foods.

Ageless Eye, Tell-Tab, and O_2 Sense are examples of commercial integrity indicators that provide color changes upon oxygen exposure so that suitable for the naked eye detection in terms of oxygen concentrations at low concentration (0.5%). Another example is Food Sentinel System™ that has been discontinued already. It is a biosensor system for the food pathogen detection using a specific pathogen antibody immobilized onto the membrane creating a barcode part (Yam et al. 2005). Here, when the contaminating bacteria are present, it will produce a localized dark bar, which, in turn, causes the error or unreadable barcode while scanning when it is used in the supermarket.

2.3 Smart Indicator for Food Freshness

Based on the type of design construction, the food freshness indicator could be grouped into (1) single indicator; (2) dual indicator; and (3) indicator array (Kuswandi 2020). The single indicator is a freshness indicator that only used one indicator to detect, sense, trace, and inform the food freshness quality and safety inside the package. The dial indicator is the freshness indicator that used two indicators in monitoring and informing the food freshness quality and safety. At the same time, an indicator array is the multiple indicators that used several indicators in an array to create a pattern in detecting or sensing, and informing the food freshness quality and safety. Mostly, commercially available freshness indicators are a single indicator type, while dual indicator and indicator array are undergoing laboratory-scale developments. Figure 2.4 shows the ripeness indicator or sensors based on design, type, and application for food freshness.

The smart indicators integrated into food packaging can act as an important tool in sensing, detecting, monitoring, and tracing food freshness quality and safety.

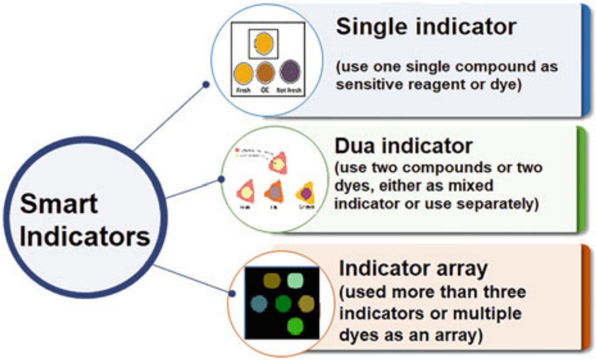

Fig. 2.4 Types of smart indicators used in food packaging for freshness monitoring

These smart indicators or sensors are critically important when foods are stored outside their desired conditions, e.g., extreme hot or cold. Furthermore, in the case of processed foods, where they should not be frozen, a smart indicator could be necessary to monitor whether they had been stored in freezing conditions improperly or not. On the other hand, a smart indicator could also inform if the processed food is sensitive to heat where it had been exposed to hot conditions and the duration involved. Moreover, the detailed description of the smart indicators for food freshness quality and safety is described in the following subsections.

2.3.1 Single Indicator

Commonly, a single indicator or sensor is used in a single color indicator construction, and the choice of reagent dye has a great impact on its colorimetric indicator performance. In order to construct high sensitivity of the colorimetric indicator or sensor, the reagent dye should have high sensitivity as well. For instance, if a single indicator works based on pH change inside the headspace of food packaging, therefore, a large pH range of the reagent dye is needed, or it should be sensitive enough to pH change and easy to distinguish its color change related to the food freshness during storage (Kuswandi 2018). By using a single indicator, simple, fast, and sensitive detection of food freshness can be performed by using a noninvasive colorimetric method detected by the naked eye. For example, it is used for fish freshness detection, where it was observed to relate well with bacterial growth trends in whiting and codfish samples, which in turn allowing real-time monitoring of fish spoilage (Pacquit et al. 2007; Kuswandi et al. 2012a, b). This single indicator allows the high potential for creating "best-before" dates where it could make improvements in the food quality evaluation of food freshness active label.

Polyaniline (PANI) could make a distinctive color change with total volatile base nitrogen (TVBN), so it is often used as a single indicator in an intelligent packaging system. A single indicator was developed based on a similar working principle based on PANI film for milkfish sample (*Chanos chanos*) freshness monitoring in the fish package headspace (Kuswandi et al. 2012a, b). This single indicator showed color changes toward a variety of TVBN produced during fish deterioration as shown in Fig. 2.5. Here, the PANI film response presented as a color change is also related to microbial activities in fish samples (*Pseudomonas spp*. and TVC (total viable count)). The single indicator or sensor allows for the real-time spoilage detection of fish either at stable or fluctuating temperatures. Furthermore, a single biosensor was developed for xanthine (adenine nucleotide degradation product in animal tissue) detection (Arvanitoyannis and Stratakos 2012). In this work, the xanthine oxide was attached to the electrodes, e.g., silver, platinum, and pencil graphite electrode (Devi et al. 2013; Dolmacı et al. 2012; Realini and Marcos 2014). Another novel single indicator was developed based on curcumin for volatile amine (TVBN) detection in shrimp (Kuswandi et al. 2012a, b). The curcumin was absorbed onto the bacterial cellulose membrane to create a sensitive indicator and edible membrane for food applications. The indicator develops color from yellow to orange and finally to

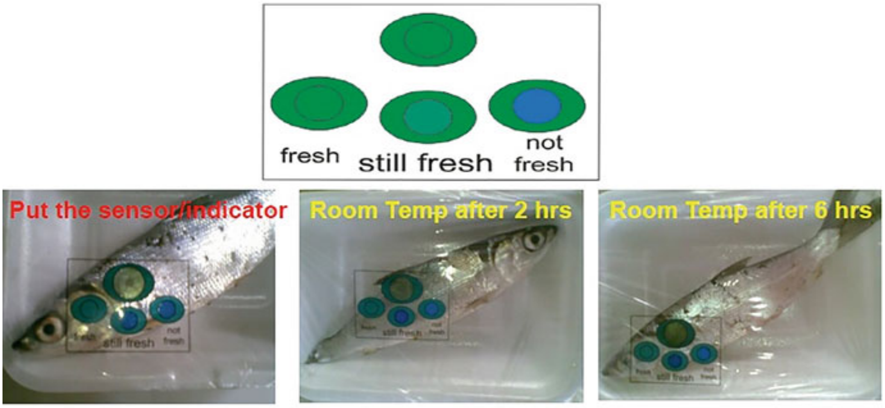

Fig. 2.5 Example of a single indicator used for fish freshness monitoring based on PANI

reddish orange for the indication of shrimp spoilage. Moreover, the indicator color change was correlated with bacterial activities in shrimp in ambient and chillier conditions.

A single indicator was constructed to monitor the guava ripeness. The single indicator was immobilized bromocresol blue on the cellulose membrane for acidic volatile compound detection. Here, when the indicator color changes from blue to green, the maturity of guava changes from ripeness to rotten (Kuswandi et al. 2013). It is often that ripeness and rotten fruit foods can be distinguished by only two color changes, since secondary ripeness fruits cannot be identified, such as medium condition. Therefore, the same group constructed a single indicator based on chlorophenol red as a ripeness indicator for the detection of grape maturity. Here, acid volatile organic compounds released during grape maturation create the indicator color development from white to beige and lastly to yellow that obviously show the ripeness, medium, and rotten grade of grape (Kuswandi and Nurfawaidi 2017).

2.3.2 Dual Indicator

Sometimes, a single indicator is difficult to distinguish the color transition in the process of color change, and therefore, mixture of two indicators could be employed to increase the sensitivity of color development end point. Dual indicator can be divided into three classes: First is to add an inert dye to the acid–base indicator, where the color does not change at the pH less than 7.0, and second is to mix the two acid–base indicators to accurately create the indicator color change in order to have a narrower range of color change by using the complementary effects of each indicator, and the last is using dual indicators simultaneously that used two indicators that referencing each other in detecting, monitoring, and informing the food freshness level, since the amount of TVBN and CO_2 in meat products is the key maker for food deterioration. Therefore, the mixed indicator color change was more obvious in the detection of TVBN at various levels of food freshness. A freshness indicator was developed based on bromothymol blue phenol red for skate fish (*Raja kenojei*) (Lee et al. 2016). Here, TVBN produced during the fish storage was increased in the fish package, causing the headspace pH to increase. As a result, the indicator changed from yellow to purple color when the fish product deteriorated.

The mixed dual indicator could also increase their sensitivity toward CO_2. The mixed dual indicator label of bromothymol blue and methyl red could accurately evaluate the skinless chicken freshness. The label works based on CO_2 detection as the main gas released by the microbial metabolism of skinless chicken. Here, when the mixed indicator shows green and orange color, it means freshness and spoilage, separately (Rukchon et al. 2014). A similar principle was developed using a mixed dye-based indicator in food spoilage for an effective shelf life detection by allowing dynamic freshness to be detected visually alongside the best-before date, which, in turn, reduces margins of error (Nopwinyuwong et al. 2010). Further applications of mixed dual indicator for food freshness indicator to other perishable food products are open up for future area of developments and commercialization.

The last type of dual indicator is dual indicators that used two indicators simultaneously as a label for food freshness monitoring. It was developed as a novel approach for food freshness monitoring, i.e., beef meat, and proposed to prevent the problem using a single indicator (Kuswandi and Nurfawaidi 2017). This is due to the fact that a single indicator is similar to traditional acid–base titration using a pH indicator dye, where it is often difficult to detect the onset of spoilage threshold, as it could be too late or too early if it is related to microbial activities on food products (Kuswandi et al. 2015). The dual indicator has several benefits as smart label, such as suitable for naked detection for the spoilage onset threshold, easily to be displayed and distinguished for each level of the food freshness as two color displays, more accurate food freshness determination, preventing false negative and positive for the level of freshness, more attractive due to two color tone as well as they referenced each other, as one indicator develops color a long side with other indicator color change. It was developed by using two pH dyes (methyl red and Bromocresol purple) to fabricate an on-package dual indicator label for the real-time detection of beef freshness (Kuswandi and Nurfawaidi 2017) (Fig. 2.6).

2.3.3 Indicator Array

Apart from single or dual indicator or colorimetric sensor, indicator or sensor array based on imaging approaches offers many benefits in nondestructive determination of food quality and safety. This imaging technique is using an indicator array or sensor array to capture a pattern of an “odor” fingerprint related to the food quality and safety (Chen et al. 2016; Morsy et al. 2016). Most of the developed indicator or sensor arrays are employed for monitoring chemical species in the food packaging headspace that are related to food freshness or spoilage of perishable foods, e.g., meat, seafood, fruits, and vegetables, which have high value. Since the cost of the sensor array is the most expensive and not simple compared to other smart indicators

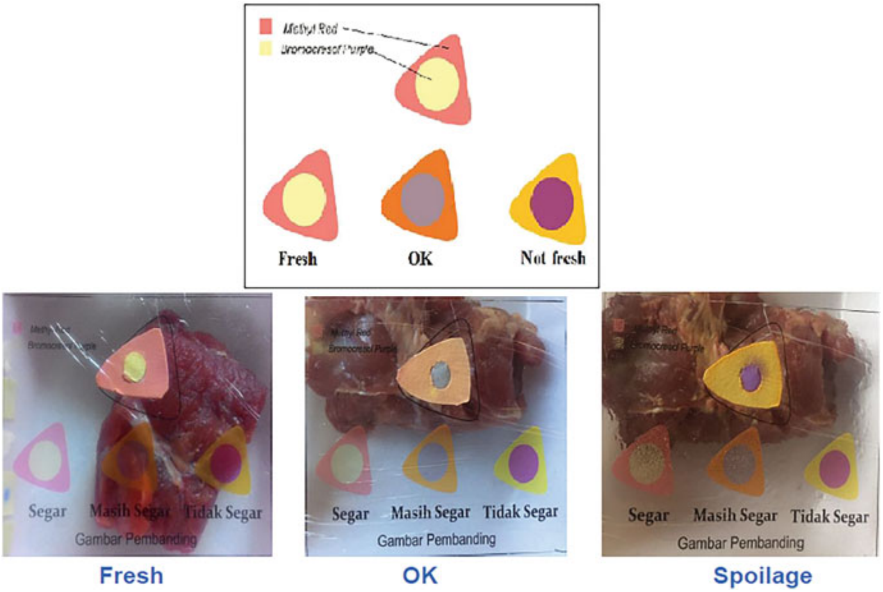

Fig. 2.6 Example of dual indicator for beef freshness packaging used two pH indicators separately

or sensors, furthermore, sensor array needs additional tools, such as smartphone or mobile device coupled with the dedicated app that have signal processing and artificial intelligence inside that used in capturing odor pattern of food related to food freshness or spoilage.

An indicator or sensor array, i.e., the electronic nose, is a system that works based on the principle of imitating or mimicking the mammalian olfactory system in a device proposed to obtain measurements that allow the classification of aroma mixtures contained in the food odor. The array creates a pattern as a specific signal to each odor, savor, or flavor. For example, e-nose contains a chemical sensor or biosensor array that specifically enables the pattern recognition of simple or even complex odor, savor, or flavor (Gardner and Bartlett 1994; Vanderroost et al. 2014b). This system was used in the quality determination of packaged beef and fresh yellow fin tuna (Blixt and Borch 1999; Dobrucka and Cierpiszewski 2014). Furthermore, it is also employed for freshness detection of broiler chicken cuts (Rajamäki et al. 2006), for the freshness of boiled marinated turkey (Salinas et al. 2014a, b), for fresh pork sausage spoilage (Salinas et al. 2014a, b), and for squid spoilage (Zaragozá et al. 2015).

Currently, the indicator array-based pH indicators and a colorimetric dye, selective for thiols, were developed for the spoilage monitoring of various meats, i.e., chicken, beef, pork, and fish, which produced the different models of the mimicking degradation pathway. The spoilage monitoring for each type of meat then followed the array color evolution using multivariate analysis by three-way PCA (principal component analysis). Using this method, it found similar protein degradation pattern

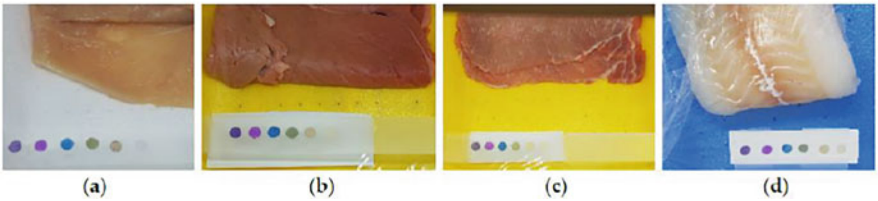

Fig. 2.7 Example of indicator array used in food packaging for freshness monitoring of numerous meats, (**a**) chicken, (**b**) beef, (**c**) pork, and (**d**) codfish (Magnaghi et al. 2020)

of meats, which can be used to monitor meat spoilage of different meats as shown in Fig. 2.7 (Magnaghi et al. 2020). Generally, the results were compared to the results of classical methods, such as sensory evaluation, microbiological assay, and headspace gas analysis. The indicator or sensor array allows for better distinctive of the food deterioration from fresh food and can be applied for different foods.

2.4 ICT for Smart Packaging

In the industrial era 4.0, ICT (Information and Communication Technology) plays a major role in our daily activities. Therefore, the use of ICT in terms of smartphones and other mobile devices has become an important part of our lifestyle. In this regard, the use of these gadgets to access and connect with many things has become obvious, including food packaging. Thus, the concept of "connected packaging" clearly will become another part of smart packaging. Of course, the term connected packaging is not only limited to food packaging but also limited to other applications in almost every kind of consumer product. It could be connected for medicines, cosmetics, category, apparel, etc. In this connected packaging, the applications could be connected with a special printed code on or within the packaged consumer products so that the consumers can activate this code with smartphones or other mobile devices to receive exclusive information regarding the content of products. In food packaging, the content could be online calorie and nutritional value, originality, halalness, etc. Hence, by applying this novel packaging concept, the smart packaging will become smarter as following applications (Fig. 2.8).

2.4.1 Artificial Intelligence

Recently, there is increasing use of artificial intelligence (AI) and machine learning (ML) for smart sensor system development for the problem-solving-based approach. For instance, online or real-time AI and ML or new algorithms are developed, and various methods are employed to integrate these algorithms in a smartphone or other mobile devices for sensor systems to allow for autocalibration measurement, enhancing linear range, etc. New clustering and classification techniques, learning methods,

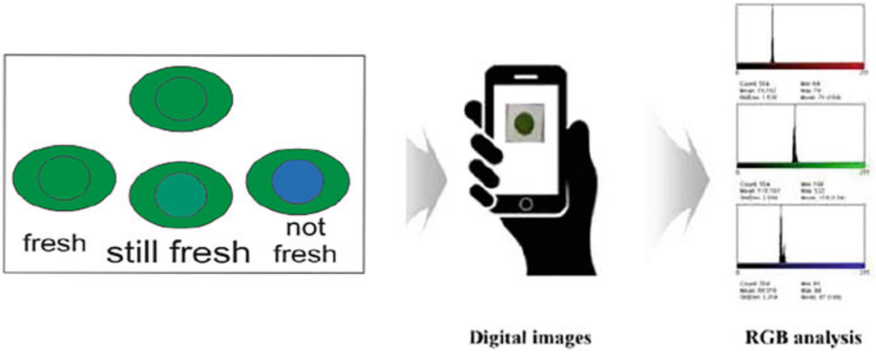

Fig. 2.8 Example of smartphone-based analysis in intelligent food packaging for food freshness monitoring

and data quality methods are required, including distributed AI algorithms to make indicators or sensors to be more accurate in the target analyte detection. For instance, the integration of an ML algorithm to a sensor based on luminescence detection has been used for time-resolved luminescence data for the detection of O_2 in the sample (Dordević et al. 2018). This approach also has great potential to be integrated into the smart packaging system, including IoT, image processing, and artificial intelligence (Schaefer and Cheung 2018). For instance, this approach was used for the protein degradation pattern of meats and was applied to monitor meat spoilage of different meats (Magnaghi et al. 2020).

Another approach that can be applied in smart packaging used a neural network (NN). For example, in food freshness monitoring using an indicator or sensor array, a NN learns to correlate the quantities image sensed by a sensor array with the analyte target concentration. In this case, as the number of measurements is limited, typically, the NN training was done with a simulated training dataset. Besides, the temperature that needs to be counted in this array was kept constant but also could be predicted. The best performing network was optimized by employing different architectures and hyper-parameter tuning. Then, the trained network was used in the data experiment to check its applicability when used to other data. The error in the freshness-level prediction was caused by the synthetic training data that were calculated using an approximate model. By employing this approach for the training dataset, the experimental data would reduce the absolute error in the freshness-level measurements. This approach was applied for the measurement of oxygen concentration, and the results were comparable with many commercial oxygen sensors based on the traditional methods (Chu et al. 2016; Michelucci et al. 2019). Moreover, the AI and ML integration support other fields, e.g., IoT, big data. Therefore, in smart packaging development, these technologies would enhance the reliability of the sensing system. In this case, the data were used to help consumer, particularly when it allows the systems to monitor and to learn indicator or sensor responses that can be related to food freshness status. Therefore, the future challenges in smart packaging development are the novel approaches to use AI algorithms via smartphone or other mobile devices in the food freshness monitoring system. This work will cover new hybrid AI systems, novel ML models, etc., that could be applied to enhance indicator or sensor array performance in monitoring of food freshness status. Moreover, AI soon can be expected to play a more important role in improving machine learning, data mining, and decision support systems that are allowed to adjust processes and decision in real time and on the basis of big data (Vanderroost et al. 2014).

2.4.2 IoT

The IoT is a concept focused on serving a global infrastructure of interconnected networks for connecting objects to the cyber world. It allows for the tracking and control of devices integrated with indicators, sensors, and actuators (Schaefer and Cheung 2018). For instance, RFID tags equipped to the packaging objects will be easily tracked along their chain from producer to customer (Cui 2016). Therefore, by the integration of smart packaging in the IoT, the product lost or damaged during shipments and distribution could potentially be prevented and reduced significantly. In few years, not only smartphones and other gadgets will be part of the IoT, other appliances, e.g., food packaging, furniture, and cars, or even machinery and factories will also become part of the industrial IoT (IIoT) (Da Xu et al. 2014).

One of the most important areas in IoT is a further advancement in intelligent food packaging technologies. It is improved in monitoring and controlling the conditions of food packaging and managing online or real time. This advancement will affect food quality and safety and food waste reduction significantly, which would increase consumer health. A suitable and reliable IIoT infrastructure and the associated ICT equipped into both the food packaging and their supply chain, generally speaking, would create cyber-physical production and delivery networks within a company and across several companies. Moreover, the further advantages from these digitalization approaches of the food product life cycle and supply chain are easy to be managed, organized, and distributed.

2.5 Conclusions

The recent advances in smart packaging, particularly intelligent packaging, depends on the smart materials development and sensor technology, wherein some way allow for direct detection or indirect detection by mimicking the packaged food freshness condition to help a customer in judging the quality of food freshness and safety, as well as its shelf life and computability. For freshness indicator or sensor, it should be compatible with printing technology for mass production, low cost over the food value, simple, user-friendly, reliable, accurate, and reproducible in their range of operation, food contact safe, and environmentally friendly.

The integration of an indicator or sensor in food packaging has created innovative ways in smart packaging developments. These innovations have allowed increasing food quality, safety, shelf life, and usability, reducing food loss and waste. Today, most packaging advances have been paved by the consumer preferences and trends worldwide, such as ICT, including imaging technology, A.I., big data, and IoT, with their numerous mobile devices. In addition, some advances have derived from the emerging technology, such as nanotechnology, the sensing technology in nanosize. Undoubtedly, novel smarter indicator or sensor in smart packaging will be a rise in the year to come as the marriage between emerging these technologies, so that the smart packaging could inform the consumers smarter, not only by the color development but also by their smart mobile devices in terms of food preferences, quality, and safety. Furthermore, smart packaging could become even smarter in the near future by numerous functions, such as tracking, tracing, authentication, preferences, online calorie, and nutritional value, halalness, and food sustainability. These functions can be covered via the connected packaging, where it allows consumers to communicate with the food product via a mobile device using an active package label or code that contains many pieces of information regarding the food products.

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3

Novel Packaging Development, Assessment and Authentication Using Smart Technologies, Non-invasive Biometric Sensory Tools and Artificial Intelligence

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Abstract

Packaging creates the first impression from consumers when selecting commercial food or beverages. Different packaging components are important as they contain all areas of interest related to branding, shape, design and nutritional information, which could determine willingness to purchase and success of products in the market. However, traditional packaging acceptability assessments based on focus groups, acceptance and preference tests may be biased and subjective. Therefore, novel assessment methods have been developed based on more objective parameters, including non-invasive biometrics such as eye tracking, emotional responses from consumers and changes in physiological parameters, such as heart rate and body temperature. Emerging technologies have also been studied for packaging assessment, such as virtual/augmented reality and artificial intelligence tools, including computer vision and machine learning modelling. Furthermore, counterfeiting has been a major issue among commercial products, with food and beverages accounting for 10% counterfeited, including packaging and branding. This chapter focuses on the latest research on

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intelligent and digital technologies for packaging development, assessing consumer acceptability towards packaging and authentication using new and emerging digital technologies.

3.1 Introduction

It is well known that 95% of new food and beverage products are deemed to fail in the market without proper evaluation in terms of consumer acceptability and liking assessments (Buss 2018; Fuentes et al. 2020; Gonzalez Viejo and Fuentes 2020). The latter is especially relevant for food and beverage packaging since it is the first contact with the product and creates the first impression among consumers. Traditionally, the design and information added to packaging have been determined by food companies hiring visual design companies to present several alternatives. Then, the best packaging design is subjectively chosen by an executive group from the food company, without any other objective measures being considered.

When including sensory science in the decision-making process for effective packaging, food companies can use either focus groups conformed by professionals in the food and beverage area or by selecting potential consumers in the respective age group the food and beverage products are targeted. More in-depth studies can be conducted using consumer testing of 3D packaging prototypes or 2D and 3D image rendering on screens. These techniques can give a more objective sense of why consumers prefer different packaging features, depending on the number of questions included in the test.

However, all these techniques are either subjective, require trained professionals or rely on the conscious responses of panellists according to several pre-set questions. Recent research has determined that human sensory perception and emotional response towards images, food and beverages are mostly determined by the response of the autonomic nervous system (ANS) (Fuentes et al. 2020, 2021a; Gonzalez Viejo et al. 2019a, b, 2020, 2021; Biju et al. 2021; Gunaratne et al. 2019a). Hence, the conscious responses to preference or packaging appeal may only render partial information for decision-making.

New and emerging technologies have been applied in recent years in an effort to tap into missing information, such as the responses of the ANS to packaging design from consumers and how different features of the packaging elicit different emotional and physiological responses that may be linked to liking and preference.

The packaging design is also important to avoid anti-counterfeiting, which is a major problem within the industry and may affect consumers' confidence when selecting a food product. It has been shown that, when incorporating anti-counterfeiting elements using different technologies from intelligent or smart packaging, consumers' trust and loyalty are reinforced (Francis 2019).

This chapter focuses mainly on these new and emerging technologies applied to packaging assessment. This includes biometrics for physiological and emotional response assessment, eye trackers, virtual and augmented reality, artificial intelligence (AI), the development of intelligent or smart food packaging as innovative additions and anti-counterfeiting solutions, and consumer acceptance assessments for these technologies.

3.2 Biometrics in Packaging Assessment

Typical assessment of consumers' responses towards packaging/labels consists of the use of acceptance tests using hedonic and just about right scales, and ranking or paired preference tests. Other scales such as 100- or 15-cm non-structured scales and check-all-that-apply (CATA) tests have also been used to assess emotional responses from consumers. However, all those methods are self-reported, which means that participants go through a thinking process for decision-making to provide their answers. This leads to subjective responses that may be affected by different types of bias, such as suggestion effect, distraction error, halo effect and cultural factors (Kemp et al. 2011; Meilgaard et al. 2006).

The use of biometrics in sensory analysis has become more popular, especially in the last 5 years, to assess consumers' responses from the ANS and their emotions (Fuentes et al. 2021a; Gonzalez Viejo et al. 2019b, c). The ANS controls the body's involuntary function, such as heart rate, body temperature, pupil dilation, respiration, skin conductance and blood pressure. Once a stimulus is received, the brain is able to integrate the information and elicit an involuntary response to the environment, which, depending on the type of stimulus, may trigger either the sympathetic (stress) or parasympathetic (resting) nervous system (Donato 2018; Silverthorn 1998). On the other hand, emotional responses depend on the release of different hormones, which are released depending on the stimuli that have been received. Some of these hormones include adrenaline and cortisol, which trigger negative emotions, and dopamine, oxytocin, and serotonin that elicit positive emotions; these are the subconscious responses. After receiving motivation, this affects the behaviour, leading to the thinking process and ending in decision-making (Smith 2015). In previous studies, these responses have been reported to be different according to consumers' cultural background, such as Asians vs Westerners. This is because the reactions to stimuli also depend on participants' previous experiences and familiarity with the products (Fuentes et al. 2020; Torrico et al. 2018a; Gonzalez Viejo et al. 2018a; Gunaratne et al. 2019b).

Most of the published studies use contact sensors placed either on the chest, extremities or head to measure the physiological responses; however, this creates awareness of the participants about being monitored and affects their ANS responses as possible creation of a stressful environment (Gonzalez Viejo et al. 2018b; Frelih et al. 2017). Therefore, some researchers have developed non-invasive techniques using video analysis to reduce bias (Gonzalez Viejo et al. 2018b, 2019b; Gonzalez Viejo Duran 2020; Mohamed et al. 2020; Jain et al. 2016). On the other hand, for the assessment of subconscious emotional responses, some commercial software has been developed such as FaceReader™ (Noldus Information Technology, Wageningen, Netherlands), Affectiva (Affectiva, Boston, MA, USA), iMotions

(iMotions, Copenhagen, Denmark) and MorphCast® (MorphCast, Florence, Italy). Furthermore, commercial eye trackers such as Tobii (Tobii, Danderyd Municipality, Sweden) and Gazepoint (Gazepoint, Vancouver, BC, Canada) have been used to assess gaze parameters such as duration and number of fixations when evaluating packaging/labels.

3.2.1 Physiological Assessment

The most common physiological responses measured while assessing packaging/labels are heart rate and skin conductance (Table 3.1). Among the latest studies using these technologies is the research from Liao et al. (2015), who assessed different elements in packaging such as the image, colours and typefaces. In this test, they assessed the self-reported responses and skin conductance of 120 participants while evaluating 12 samples. The authors used two sensors (Procomp2, ThoughtTech, Montreal, Quebec, Canada) attached to the middle and index fingers of the left hand of participants to measure skin conductance. The main findings consisted of significant differences ($p < 0.05$) in skin conductance between samples with a negative image and without any image. Cuesta et al. (2018) assessed consumers' physiological response based on skin conductance towards four types of packaging with different colours and areas of interest (AOI). The authors did not report the method or sensors used to assess skin conductance, but it was claimed that a similar skin conductance response was obtained for all samples. However, no statistical analysis was reported. Rodriguez-Escudero et al. (2019) evaluated four different label layouts (changes in size and location) of smoothies' packaging and recorded skin conductance of 42 participants using electrodes (Bitbrain Technologies, Zaragoza, Spain) attached to the fingers of the left hand. The authors converted the skin conductance results to two parameters: activation and impact, and found significant differences between samples for both variables at $p < 0.05$ and $p < 0.01$. Modica et al. (2018) conducted a study using chocolate and rice packaging to assess consumers' heart rate and skin conductance responses towards different brands (major vs private label), hedonic value (comfort vs daily food) and familiarity (foreign vs local products). The authors used a pulse oximeter placed on the thumb of participants to measure heart rate and Shimmer electrodes (Shimmer Sensing, Dublin, Ireland) placed on the non-dominant hand for skin conductance. However, no results were reported for these parameters.

Schulte-Holierhoek et al. (2017) evaluated milk packaging with different colours to assess heart rate and skin conductance responses from consumers of different nationalities. The authors used the Vrije University Ambulatory Monitoring System (VU-AMS, ver. 3.9) (Willemsen et al. 1996). Heart rate was measured using the electrocardiogram method with seven electrodes (Kendall™ ECG Electrodes; H98SG; Cardinal Health, Dublin, OH, USA) attached to the chest, while for skin conductance, electrodes attached to the index and middle fingers of the non-dominant hand were used. For heart rate, significant differences ($p < 0.05$) were found between responses from participants according to their nationality. Skin

Table 3.1 Summary of recent studies using biometrics in the assessment of consumer responses towards food packaging

Food packaging	Assessment elements	Biometrics	Method	Number of consumers	Number of samples	Time of image display	Main findings	References
Physiological responses								
Chocolates	Images Typefaces Colours	SC	Attached sensors Fingers	120	12	6 s	Significant differences ($p < 0.05$) between packaging with negative image and no image	Liao et al. (2015)
Juice	Colours Areas of interest	SC	NR	35	4	10 s	Similar results for all samples	Cuesta et al. (2018)
Smoothies	Label layout	SC	Attached sensors Fingers	42	4	2 s	Significant differences ($p < 0.05$; $p < 0.10$) between samples with different layout	Rodríguez-Escudero et al. (2019)
Chocolate Rice	Brand (major vs private) Familiarity (local vs foreign) Hedonic value (comfort vs daily food)	SC HR	Attached sensors: – Palm – Thumb	32	8	15 s visual 15 s interaction	NR	Modica et al. (2018)
Milk	Colours	SC HR	Attached sensors – Fingers – Chest	98	4	10 s	At ($p < 0.05$): SC higher in red vs blue packaging SC lower in low vs high popularity HR significant differences based on nationality of consumers	Schulte-Holierhoek et al. (2017)

(continued)

Table 3.1 (continued)

Food packaging	Assessment elements	Biometrics	Method	Number of consumers	Number of samples	Time of image display	Main findings	References
Healthy product	Virtual vs physical packaging	SC HR	Attached sensors – Palm – Finger	83	6	11 s	SC and HR correlations ($p < 0.01$; $r > 0.90$) between virtual and physical assessment	Vila-López et al. (2021)
Healthy product	Colours and design/message	SC	Attached sensors – Palm	83	6	11 s	SC ratio significantly lower in blue packaging	Vila-López and Küster-Boluda (2019)
Emotional responses								
Juice	Colours Areas of interest	Emotions	NR	35	4	10 s	Packaging with yellow colour higher in positive emotions	Cuesta et al. (2018)
Chocolates	Images Typefaces Colours	Emotions (valence)	Attached sensors face	120	12	6 s	Significant differences ($p < 0.05$) between packaging with positive image and no image	Liao et al. (2015)
Yoghurt	Recyclable logos (recyclable, non-recyclable, no logo)	Emotions	FaceReader™	89	6	6 s	More positive emotions towards samples with recyclable logo	Songa et al. (2019)
Snacks	Spatial representations (foreground vs background)	Emotions	FaceReader™	40	Study 1: 4 Study 2: 4	60 s	Foreground representation elicited higher happiness, while background had higher sadness	Vergura and Luceri (2018)

Olive oil	Health claims	Emotions (arousal)	FaceReader™	80	4	60 s	Interaction between perceived happiness and arousal	Pichierri et al. (2021)
Milk	Materials/shapes/colours	Emotions	FaceReader™	50	6	30 s	Significant differences ($p < 0.05$) between emotions for each sample	Clark et al. (2021)
Chocolate	AOI Familiarity (novel vs familiar packaging)	Emotions	FaceReader™	60	12	10 s	Significant differences ($p < 0.05$) between samples in sadness for novel packaging More positive emotions elicited by the brand name AOI	Gunaratne et al. (2019a)
Coffee	Packaging concepts (bold, every day, fun, premium, classic, natural)	Emotions	Computer app based on Affectiva	69	6	15 s	Positive emotions related to everyday concept Valence related to premium concept Negative emotions related to bold concept	Gonzalez Viejo et al. (2021)
Eye tracking								
Juice	Colours AOI	Fixation path Fixation time	Tobii ET	35	4	10 s	Assessment starts in the centre of packaging, then top (logo) and finish in the bottom (text)	Cuesta et al. (2018)
Smoothies	Label layout (AOI)	Fixations	Tobii ET	42	4	2 s	The “cold press” claim and product name had high fixations regardless of the position	Rodríguez-Escudero et al. (2019)
Yoghurt	Recyclable logos	Pupil diameter Eye movement	SMI-RED250 ET	89	6	6 s	Larger pupil diameter with samples with recyclable logo	Songa et al. (2019)

(continued)

Table 3.1 (continued)

Food packaging	Assessment elements	Biometrics	Method	Number of consumers	Number of samples	Time of image display	Main findings	References
Chocolate	AOI Familiarity (Novel vs familiar packaging)	Fixation duration Number of fixations	Gazepoint ET	60	12	10 s	Higher number of fixations in the image and brand of familiar samples Higher number of fixations in country of origin, ingredients and manufacturer of novel packaging	Gunaratne et al. (2019a)
Baby formula (thermochromic label)	Colour transitions in different location (brand plus Koala image and snowflake image)	Fixation duration Number of fixations	Eye tribe tracker	40	3	7 s	Brand plus Koala image had significantly ($p < 0.05$) higher fixation time and number of fixations than other samples	Torrico et al. (2018b)
Olive oil dressing	Label Packaging type	Eye fixations	RealEye system Real-time video analysis	15	6	NR	Higher fixations in product name, image and country of origin In transparent bottles, fixations are also high in the neck and cap of bottle	Fazio et al. (2020)
Wine	Bottle design	Fixation time Time to first fixation	Tobii ET	37	8	7 s	Classic wine bottles had higher general visibility	Merdian et al. (2020)

Yoghurt	Nutrition claims	Fixation time Fixation count	Tobii ET	100	251 labels 6 nutrition claims	15 s	Higher fixation time in low-sugar claim	Ballco et al. (2019)
Apples	Organic labels	Fixation time Fixation count Number of visits	Tobii Pro Glasses 2 ET	73	6	NR	Visual attention related to preference and product choice	Meyerding and Merz (2018)
White wine	AOI	Fixation time Visual attention	SMI-RED250 ET	44	7	10 s	Highest visual attention to award star rating Lowest visual attention to sweetness, vintage and country of origin	Mokrý et al. (2016)
Organic food	AOI	Fixation time Visual attention	SMI-RED250 ET	Group 1: 88 Group 2: 59	Group 1: 9 Group 2: 9	NR	Higher visual attention to brand, image and organic claims	Drexler et al. (2018)
Gluten-free cookies	Gluten-free claims	Dwell time Revisits Fixation count Average fixation duration Visual attention	SMI ET glasses 2 wireless	67	5	7 s	Significantly ($p < 0.05$) higher attention to verbal (text) than non-verbal (graphic) organic claims	Sielicka-Różyńska et al. (2021)

(continued)

Table 3.1 (continued)

Food packaging	Assessment elements	Biometrics	Method	Number of consumers	Number of samples	Time of image display	Main findings	References
Soda	Warning sugar labels	Fixation time Fixation count	SMI Mobile remote ET	180	2	10 s	Significantly ($p < 0.01$) lower dwell time in non-warning AOIs in samples with warning sign	Popova et al. (2019)
Potato chips	Colour and text	Time to first fixation	SMI-RED250 ET	24	8	15 s	Participants initially fixate on the colour	Huang et al. (2021a)

NR not reported, *SC* skin conductance, *HR* heart rate, *ET* eye tracker, *AOI* areas of interest conductance was significantly higher when evaluating red rather than blue packaging, while it was lower when assessing packaging with low popularity. On the other hand, Vila-Lopez et al. (Vila-López and Küster-Boluda 2019; Vila-López et al. 2021) published two papers using the same low-fat food packaging samples with different colours (black, blue and red) and design/message (added a small drawing). In both publications, the authors measured skin conductance of 83 participants using a PowerLab/16SP electrode (AD Instruments, Sydney, NSW, Australia) attached to the palm of the non-dominant hand; however, for the second publication, heart rate was included, and it was measured using a PowerLab/16SP electrode (AD Instruments, Sydney, NSW, Australia) attached to the finger. In the first paper, the authors reported that the skin conductance was significantly ($p < 0.05$) lower when evaluating blue packaging samples. In their second paper, they compared results when evaluating the packaging virtually and physically and found that for heart rate and skin conductance there was a positive and significant ($p < 0.01$) correlation ($r = 0.90$).

As highlighted by previous research, there is an opportunity to conduct research and develop new methods in consumer evaluation towards food packaging using non-invasive biometrics to assess physiological responses to avoid the bias generated by contact sensors. There are novel techniques developed to measure heart rate and body/skin temperature using computer vision to assess food and beverages (images, videos and tasting). The heart rate method consists of recording videos of participants using the BioSensory Application (App; The University of Melbourne, Parkville, VIC, Australia) while evaluating the products. The videos are analysed using computer vision algorithms developed in MATLAB® (MathWorks Inc., Natick, MA, USA) using the photoplethysmography (PPG) method based on the luminosity changes in the forehead and cheeks produced by the blood flow (Gonzalez Viejo et al. 2018b; Fuentes et al. 2018). On the other hand, the contactless body/skin temperature method consists of using a thermal infrared camera integrated with the BioSensory App that can capture thermal images to assess consumers' temperature changes when evaluating the samples. These are then automatically analysed using MATLAB® to obtain the maximum temperature of the eye section (Gonzalez Viejo et al. 2018c, 2019a).

3.2.2 Emotional Assessment

Recent studies have used the subconscious assessment of emotions from consumers when evaluating food packaging/labels (Table 3.1). While the traditional technique uses sensors attached to specific muscles in the face to assess facial movements, more recently, the most common method is the non-invasive video analysis using commercial software. The software used to analyse videos for emotions works by automatic face detection and recognition of features such as eyebrows, mouth, eyes and nose. Once these are identified, the software can track the features identifying the micro- and macro-movements, through the duration of the video, using a specific model or algorithm developed by each software, such as an active appearance model in FaceReader™ and histogram of an oriented gradient in Affectiva. Then, these are translated into emotions such as happy, sad, joy, contempt, angry and scared using machine learning models based on artificial neural networks (ANNs) in FaceReader™ and support vector machine (SVM) in Affectiva. This non-invasive automatic process is convenient to assess emotional responses towards stimuli such as food packaging/labels, as consumers are not aware of the video recording throughout the study, making them have more natural/spontaneous reactions when evaluating the stimuli and, therefore, reduces bias.

Authors such as Liao et al. (2015) still use the traditional method of attaching two electrodes to the muscles above the left eyebrow using the Procomp2 sensors; however, this technique only measures the valence of emotions. This study found that chocolate packaging with a positive image elicited significantly higher valence than those with no image; the authors also found that the results from this analysis were different from those self-reported for emotions. As mentioned before, this may be due to consumers' awareness of being monitored with the attached sensors. Therefore, authors such as Songa et al. (2019) conducted a study with yoghurt packaging to assess consumers' emotional responses to recyclable logos (recyclable, non-recyclable, no logo) included in labels. This was conducted using FaceReader™ 5, which is capable of analysing facial expressions and translate them into emotions such as happy, sad, angry and surprised. The authors found that packaging with the recyclable logo elicited more positive emotions. Similarly, Vergura and Luceri (2018) evaluated spatial representations of packaging from different snacks (biscuits, focaccia, crackers and cake) by placing the product representation in the foreground and background to assess consumers' emotional responses. Authors also used the FaceReader™ 5 to analyse the videos from consumers while assessing the samples, and it was found that there were significantly ($p < 0.05$) more positive emotions (happiness) for the foreground and higher sadness for the background representation.

Pichierri et al. (2021) evaluated four samples of olive oil packaging with different health claims and assessed consumers' emotions analysed using FaceReader™. However, the authors only focused on the arousal value and discarded any other parameters provided by the software. They found an interaction between the perceived healthiness and arousal. Clark et al. (2021) also used FaceReader™ to assess emotional responses from consumers, but with a different objective, as they displayed milk packaging samples with different materials/colours and no label. They did not find significant ($p < 0.05$) differences between samples for any emotion, but there were significant differences between emotions for each sample. Gunaratne et al. (2019a) used the BioSensory App to gather self-reported responses and videos from consumers when evaluating chocolate packaging (six familiar and six novel). The authors also focused on assessing consumers' emotional responses towards different AOI (brand, ingredients, manufacturer, nutrition facts, net content and bar code). The videos from consumers were analysed using FaceReader™ and found significant differences ($p < 0.05$) between samples from the novel packaging for sadness. The authors also found that more positive emotions were elicited by the brand AOI of novel packaging. On the other hand, Gonzalez

Viejo et al. (2021) evaluated six different coffee pods packaging designed with different concepts (bold, fun, premium, classic, natural, everyday) based on the TNS NeedScope model™ (NeedScope International, Auckland, New Zealand). The authors used a novel virtual method to conduct the sensory session using Zoom (Zoom Video Communications, Inc., San Jose, CA, USA) and Google Forms (Google, LLC, Mountain View, CA, USA) to display the questionnaire and record consumers' reactions during the test. These videos were analysed using a computer application developed by the Digital Agriculture Food and Wine Group from the University of Melbourne, Australia, based on the Affectiva (Affectiva, Boston, MA, USA) software development kit (SDK). Results showed that positive emotions were related to the everyday packaging concept, valence with the premium sample and more negative emotions were associated with the bold packaging.

3.2.3 Eye Tracking

Eye tracking is the most used biometric method to assess consumers' subconscious responses towards food packaging/labels (Table 3.1). This is, generally, a non-invasive or contactless method, except for the alternative of eye tracking glasses, which are often used as a portable method when the test is conducted in an external location. Eye trackers are composed of camera-based sensors with an integrated infrared light that can detect the eyes and pupils. Once these are detected, it can follow and measure the gaze movements and positioning, and pupil size (Gonzalez Viejo et al. 2018c, 2019b; Torrico et al. 2018b). Using specific software connected to the eye tracker, different parameters such as fixation duration, the number of fixations, time to the first fixation and pupil dilation can be determined (Table 3.1). Fixation duration refers to the time spent looking at a specific location or AOI and is related to the importance that consumers give to the specific elements in the sample (Torrico et al. 2018b; Merdian et al. 2020). The number of fixations is used to assess how many times the participants fixate in a specific AOI during the test and is related to the importance that consumers give to the AOI (Torrico et al. 2018b; Meyerding and Merz 2018). Besides, the time to first the fixation is the time that participants take to fixate in a specific AOI for the first time (Merdian et al. 2020). On the other hand, pupil dilation refers to the pupil size and its changes during the evaluation of the samples; when it is more dilated, it has been associated with negative stimuli or emotions (Oliva and Anikin 2018; Shechner et al. 2017). The eye trackers can also obtain qualitative data such as heat maps and fixation maps to assess the areas of higher visual focus and the path or order in which the sample was evaluated.

The most used eye trackers among the recent publications are the Tobii (Cuesta et al. 2018; Rodríguez-Escudero et al. 2019; Merdian et al. 2020; Meyerding and Merz 2018; Ballco et al. 2019), and SMI eye trackers (SensoMotoric Instruments, Teltow, Germany) (Songa et al. 2019; Mokrý et al. 2016; Drexler et al. 2018; Sielicka-Różyńska et al. 2021; Popova et al. 2019; Huang et al. 2021a), and, to a lesser extent, Gazepoint (Gunaratne et al. 2019a), The EyeTribe Tracker (The

EyeTribe©, Copenhagen, S. Denmark) (Torrico et al. 2018b) and the RealEye System (RealEye, Poznań, Poland). The latter consists of an online software program capable of tracking eye movements in real time using a computer-integrated webcam (Fazio et al. 2020). The number of consumers recruited for the tests in the recent publications varied from 15 to 180, while the number of samples ranged from 2 to 251, and the time used to display the stimulus is within 2–15 s (Table 3.1). However, the experiment must be carefully designed to avoid any possible bias in the results; in this context, using 251 samples for a test (Ballco et al. 2019) is too large and may cause consumers' fatigue. Furthermore, displaying the stimulus for 2 s (Rodríguez-Escudero et al. 2019) may not be enough time for the participants to evaluate the sample. The studies mentioned in Table 3.1 were mainly conducted in packaging belonging to (1) beverages (Cuesta et al. 2018; Rodríguez-Escudero et al. 2019; Merdian et al. 2020; Mokrý et al. 2016; Popova et al. 2019), (2) snacks (Gunaratne et al. 2019a; Sielicka-Różyńska et al. 2021; Huang et al. 2021a), (3) yoghurt (Songa et al. 2019; Ballco et al. 2019), (4) organic food (Meyerding and Merz 2018; Drexler et al. 2018) and others such as baby formula (Torrico et al. 2018b) and olive oil dressing (Fazio et al. 2020). Furthermore, these publications focus on the assessment of mainly four elements such as (1) claims (Songa et al. 2019; Meyerding and Merz 2018; Ballco et al. 2019; Sielicka-Różyńska et al. 2021; Popova et al. 2019), (2) AOI or layout (Gunaratne et al. 2019a; Cuesta et al. 2018; Rodríguez-Escudero et al. 2019; Mokrý et al. 2016; Drexler et al. 2018), (3) colours (Cuesta et al. 2018; Torrico et al. 2018b; Huang et al. 2021a) and (4) design (Merdian et al. 2020; Fazio et al. 2020). More recently, Fuentes et al. (2021b) presented a novel and integrated method that allows assessing subconscious emotional and eye tracking responses towards each AOI from packaging and labels using non-invasive biometrics. This method eases the interactive and real-time evaluation and re-design only of the specific AOIs that require any modifications, rather than the entire label. This method has the capability of integrating other ANS responses such as heart rate, blood pressure and skin temperature to obtain more responses from consumers.

3.3 Virtual and Augmented Reality

Two main types of reality, virtual and augmented, have been developed to either modify the environment, create scenarios or incorporate virtual elements in real-life environments or objects. Virtual reality (VR) consists of a 3D environment or scenario presented through a headset covering the eyes to isolate the subject from the real situation. On the other hand, augmented reality (AR) combines virtual or digital 2D or 3D images or animations overlayed in the real objects or environment. This is often through special glasses such as the Microsoft HoloLens (Microsoft Corporation, Redmond, WA, USA) or devices such as smartphones (Fuentes et al. 2021a; Djurdjevic et al. 2019; Crofton et al. 2019). The third type of reality, named mixed reality, has been developed, consisting of a combination of a VR environment displayed using an AR device that allows mixing both the real and virtual environments with interaction (Fuentes et al. 2021a). However, it has not been used much in food packaging evaluation.

Using VR technology, stores have been created to experience the store environment without going to the physical place. This environment allows customers to virtually walk through the store aisles, browse the products through the shelves, see their position and use a controller to pick the products, read the label and add them to the cart for purchasing (Lombart et al. 2020; Siegrist et al. 2019). In VR stores, the packaging acquires higher importance because consumers cannot touch, assess freshness, look at the expiry date or smell the product; therefore, the visual aspects become the sole driver of purchase decision-making. In this context, VR is a very convenient tool for product development. It allows researchers and developers to conduct consumer tests to assess the acceptability of the prototypes and easily modify the packaging characteristics according to consumers' feedback (Lombart et al. 2020). Virtual reality may also help assess whether the success or failure of a product may be due to its packaging or its position on the shelves in a virtual store without the need to take consumers to the supermarket for testing.

Some researchers have explored whether the physical and VR store experiences are similar to assess if conducting VR tests is reliable. Siegrist et al. (2019) conducted a test with 68 participants in a physical and VR store with 33 cereal products and instructed consumers to walk through the store and pick the products to read the nutritional label. The authors found no significant differences ($p > 0.05$) between the VR and physical environments in consumers' browsing behaviour and the number of times they looked at the nutritional labels. Similarly, Xu et al. (2021) assessed the behaviour of 98 consumers in physical and VR environments when looking for cereals asking them to rate their perceived healthiness. Participants were also asked to walk through the aisles and interact with the product using a controller. Results from both environments were highly correlated ($r = 0.91$) when rating the cereals according to the perceived healthiness, but also found that participants took longer evaluating the products in VR. Pizzi et al. (2019) evaluated 95 confectionery products displayed on supermarket shelves in physical and VR environments. In this study, 50 consumers participated in the study, and results also showed that the sample assessment and consumers' behaviour in both settings are comparable. On the other hand, Huang et al. (2021b) conducted a session with 80 participants to evaluate eight potato chip samples. The study aimed to assess consumers' behaviour when browsing for potato chip packaging with flavour–colour congruency and incongruency using a VR headset to walk through the store aisle and look at the products on the shelves. It was found that consumers were less efficient locating the incongruent flavour–colour packaging.

Augmented reality has been integrated into food packaging by incorporating an element in the product, such as an image or quick response (QR) code that can be read with any smartphone camera. This is then able to display a virtual object, image, animation or game overlayed with the real product so that consumers can interact with it in real time. This is used at purchasing or at home to provide more information about the product such as nutritional facts, cooking instructions, freshness of the product, country or region of origin, display animated characters, and educational content or games (Djurdjevic et al. 2019; Yang 2019). These technologies applied to packaging have also been used as anti-counterfeiting solutions as consumers can assess their authenticity by scanning the packaging before purchasing them. Some examples of products in the market with AR integrated into their packaging are Kellogg's cereals, which display mini-games and quizzes as educational tools for kids when using a smartphone. Likewise, Nesquik cereals display content for entertainment and learning when pointing the smartphone camera to the packaging. On the other hand, in 2016, McDonald's launched an AR app in the UK to display an advent calendar when pointing the camera at their products; this displayed different games, filters, vouchers and animations every day (Konopelko 2019). In Australia, McDonald's released an AR monopoly game that could be played with each product purchase, and consumers could win different prizes (Tran 2020). To test the usefulness of AR in food packaging, Sonderegger et al. (2019) conducted a test with 84 participants to compare AR and static information in a smartphone when consumers assessed five food products' nutritional and environmental information. The authors found that the participants learned more about the product when using the AR version.

3.4 Intelligent Food Packaging

The term smart or intelligent is interchangeable when it comes to packaging technology. This refers to the use of embedded sensor technologies in the packaging (Francis 2019). Food packaging materials play several important roles in transport and delivery to the consumer and are predominantly made of plastics. The advantages of plastic over other materials are its ability to block pathogens, moisture and gases depending on the type of food being delivered. Active packaging involves the ability for the product to actively deter degradation and prolong the lifetime of the foodstuff. However, the consumer is often unaware of these technologies, despite the important role they play in fighting against food spoilage, counterfeiting and supply chain tracing.

Covert intelligent technologies designed to manage the supply chain include anti-counterfeiting technologies such as invisible UV inks, DNA tracking or small compounds known as taggants concealed within the packaging for detection by specialized instruments. The Australian plastic banknote, first released in 1988, is one good example that incorporated many security devices, some overt including holograms, intaglio features, microprinting and fluorescent inks, while others remain covert (Australia TRBo 2021). In its first release, its acceptance by the public was 48%, with 26% disliking the new technology, while today, with the gradual decline in cash, the public has come to accept this diminishing form of currency (Prime and Solomon 2010).

3.4.1 Data Loggers

Intelligent technologies designed to inform the supply chain from the producers to the retailers often use relatively expensive data loggers. Here devices are included with a bundle of products to track such things as the location, temperature and humidity over time and can be communicated at all stages of the supply chain through near-infrared (NIR)/radio frequency identification (RFID), ultra-high frequency (UHF) light-emitting diode (LED) or simple universal serial bus (USB) data storage.

The majority of intelligent or smart packaging, on the other hand, are deliberately designed to inform the consumer of the quality of the food contained within, guide them in the best storage for consumption temperature, identify its authenticity or whether the packaging has been improperly tampered with or adulterated. Overt intelligent food packaging is designed to be obvious and requires little interaction to understand the information triggered or contained within the device. In addition, the removal or absence of these technologies on a package can indicate a tampered or substituted product or that it is counterfeited.

3.4.2 QR Codes

A common form of communicating product information is the addition of a QR code, which can be linked to online information about the product, promotions, advertising or use-by-date information. It could also be used for product recall in a safety breach simply by changing the online information linked to a separate set of QR codes.

Consumers have become familiar with this form of intelligent technology. Generally, consumers accept the presence of these technologies in their day-to-day life, with QR codes being routinely used for things such as movie tickets and sporting event entry being scanned directly from their phones. Although consumer awareness of QR codes has gradually increased since their initial applications, the use of this technology has had a slower increase. Consumer surveys on the use of QR codes on the packaging have seen a gradual increase in their awareness and acceptance. However, in one survey, it was shown that, depending on the type of content the consumer could access, this might be a reason not to use the technology in the future (Cox and Shiffler 2014). In a 2019 survey of tourists visiting Serbia, the impact of QR codes linked to hospitality venues was studied. The majority of the respondents were satisfied with the technology and the information it garnered; however, the overall satisfaction of the destination was more likely due to the venue itself and other local factors (Vuksanović et al. 2021). In a targeted survey with 240 young Indian adults, the majority were aware and used QR codes, while 46% scanned for fun and 40% scanned for information (Chandramouli Rajaiah 2017). However, the nature of the product would be expected to be a large factor in its use.

With the appearance of COVID-19 worldwide and the advantages gained by social distancing, QR codes have been successfully used for contact tracing (Chen

2021; Faggiano and Carugo 2020; Wu et al. 2021; Li and Guo 2020). This allows the health authorities to track those who have contracted the virus and the people they have come in contact with. In Australia, for example, this has led to people routinely registering with a QR code at every venue they frequent. In the light of social distancing rules, restaurants have used QR codes to allow for contactless ordering of food while remaining seated and distanced from other patrons (Patil and Karekar 2019). According to Rogers' adoption model of new products (Rogers 1976), the uptake is led by innovators, early adopters, followed by the early and late majority and, finally, laggards. With new technologies such as intelligent packaging, gender and age affect the category of adoption for each group. In a study on the perception of active and intelligent packaging of European Consumers, Tiekstra et al. (Tiekstra et al. 2021) chose the generation Y respondents to validate their findings since they represent an important population segment. Advertisers recognizing that they are economically valuable, that abandoned their existing methods to this cohort and are expected to become richer over time represent an important potential market. This concurs with the findings by Erika et al. (2020), who determined using the Kano model a fear of packaging innovation by older responders, although they had the highest need for such technology. Careful selection of consumer groups can be used to either enhance and target specific innovator groups or enhance and improve trust and understanding among the majority and laggards of the population.

3.4.3 Chromic Sensors and Indicators

The recent development of chromic (colour changing) sensors and indicators for the food industry has produced sensors placed outside the packaging, which actively monitor and display various food attributes. These sensors can also be used to identify substituted products, in the case of irreversible sensors, or where removed or absent may be an indication of counterfeiting. The area has grown to include several scientific approaches, including colour changing sensors triggered by changes in pH (Alizadeh-Sani et al. 2020; Liu et al. 2019) (halochromism), temperature (Liu et al. 2020a) (thermochromism), humidity (Moustafa et al. 2021) (hydrochromism), mechanical forces (Qiu et al. 2019) (mechanochromism), light (photochromism), bacterial growth (Weston et al. 2021a) (biochromism) or the passage of time (chronochromism) (Zhang et al. 2013). Of these technologies, a range of commercial examples has been used with great success. The most notable of these was the inclusion of a thermochromic sensor onto the outside of the Coors beer can that changed colour when chilled to the correct consumption temperature. The consumer acceptance of this product increased sales of this product by 3% in 1 year attributed to the intelligent technology alone (Alsever 2009). A summary of some commercial examples of intelligent technology sensors for the food industry is listed in Table 3.2. The most prolific of these sensors on the market is the freshness/integrity indicators, thermochromic inks and time–temperature indicators (TTIs). These devices are preferred to be used on impermeable containers such as glass or metal to stop the migration of inks or chemicals to the food within or contain a suitable barrier where paper and plastic are insufficient. For freshness indicators that

Table 3.2 Commercial examples of Intelligent Packaging Technologies

	Trigger	Commercial example	Company
Freshness/ integrity indicators	Degradation gases	Fresh Tag	COX Technologies
		ripeSense	ripeSense™ ad ort Research
		Food Fresh	Vanprob
	Oxygen gas	O2xyDot®	OxySense
		Ageless Eye®	Mitsubishi Gas Chemical Inc.
		O_2Sense™	FreshPoint Lab
		Tell-Tab	IMPAK
		O2 Sense™	FreshPoint Lab
	Pathogens	Food Sentinel®	SIRA Technologies
		SensorQ®	DSM NV and Food Quality Sensor
	Polymer degradation	Mimica Touch®	Mimica Lab
	Toxin antibodies	Toxin Guard™	Toxin Alert
Time-temperature indicators	Enzymatic degradation	FreshTag™	VITSAB International AB
		Checkpoint®	VITSAB
	Polymerization	Fresh-Check®	Temptime Corp.
		HEATmarker®	Temptime Corp.
	Diffusion	WarmMark	ShockWatch
		Monitor Mark™	3M Company
		Novas®	Insignia Technologies Ltd
		Tempix®	Tempix AB
		Timestrip® Plus™	Timestrip Plc
	Photochromic	ONVU™	FreshPoint and Ciba
		Lay's Chips	Chromatic Technologies (CTI)
	Fluorescent	Glow in the Dark Products	Chromatic Technologies (CTI)
	Biological	TRACEO®	Cryolog
Thermochromic inks	Temperature	Coors Beer	Chromatic Technologies (CTI)
		Thermax®	LCR Hallcrest
		Paint, Hypercolor T-Shirts	Matsui Int. Comp., Inc.
		Colour-Therm	Colour-Therm

(continued)

Table 3.2 (continued)

	Trigger	Commercial example	Company
Temperature data logger	Radiofrequency identification technologies	CS8304	Convergence Systems
		Intelligent box	Mondi Pic
		PakSense Express	PakSense
		K1-2: ESCREC014	Cryopak (tiptemp.com)
Time-temperature data logger	Ultra-high-frequency LED	TempTRIP	TempTRIP LLC

are triggered by the product themselves, such as those relying on pathogen, toxin, gas or oxygen release, alternative non-toxic sensors are required that avoid the safety issues associated with their components (Liu et al. 2019, 2020a, b; Seeboth et al. 2013). Many critical reviews of intelligent food packaging in the food industry have been reported covering both the commercial and research-based technologies currently being developed. These reviews go into great detail about the mechanism of these devices and their advantages and disadvantages, including their safety, cost and accuracy (Firouz et al. 2021; Fang et al. 2017; Biesuz and Magnaghi 2021; Weston et al. 2021b).

3.4.4 Consumer Acceptance of Intelligent Packaging

A systematic review of consumer perceptions of smart packaging was reported by Young et al. in 2020, including 28 studies (Young et al. 2020). The models used in these studies included the Siegrist risk/benefit model (five studies on nanopackaging), Kano model (five studies from one group), value-driven model (one study), the relationship between neophobia and acceptance of food technology (one study on nanopackaging), random utility theory (two studies on nanopackaging) and the theory of planned behaviour (two studies on meat products), while 13 studies did not cite any theories or models. Familiarity is generally low for active and intelligent packaging, which is not countered by educational communication. Well-known brands' awareness can help reduce the risk perception and increase acceptance. Five studies were cited, which identified that the provision of information to consumers about the packaging technology would increase trust, improve attitude and reduce the perceived risk. They concluded that the acceptance of intelligent and active packaging is not a well-researched area and should include more longitudinal studies, a broader geographical spread, specific examples and "real" applications and consumer responses to specific food groups. This was confirmed by Li et al. (2020), who showed that, when presented with product-specific applications, the approval of intelligent packaging increased. They also reiterated that surveys should be specific about the type of product group, for example, cheese and specific types of intelligent packaging; TTIs should be conducted to lead to “rich detail and industry-relevant results”.

Regional surveys of consumers on the perception of intelligent packaging have included geographical surveys from China (Li et al. 2020), Slovakia (Erika et al. 2020; Loucanova et al. 2019), Latvia (Kocetkovs et al. 2019), Italy, Europe (Tiekstra et al. 2021; Pennanen et al. 2015) and Turkey (Aday and Yener 2015) with varying findings.

A survey conducted in the different regions of Lativa in 2019, with 865 respondents, determined how familiar they were with the terms intelligent and smart packaging (Kocetkovs et al. 2019). The results showed that the majority of respondents had insufficient knowledge or understanding about smart packaging. However, it did show that there has been a decrease in the percentage of respondents not willing to pay more for innovative packaging, from 29% in 2017 to 6% in 2019. The report suggested that if customers were introduced to these new technologies through trust, comfort and satisfaction, there would be an improvement in perception and an increase in willingness to use smart packaging. These findings were similar to that of Slovak consumers that, in 2019, the results indicated they had a low level of awareness of intelligent packaging overall (Loucanova et al. 2019) and as an ecological innovation in the context of the bioeconomy (Erika et al. 2020).

In an earlier publication in 2013, consumers were tested for their acceptance of “Innovative packaging”. The terms intelligent and active packaging were not used yet; the questions specifically targeted each category. In that study, 265 Turkish respondents were asked 24 multiple-choice questions. Here, homogeneity analysis was used to determine, among other findings, that intelligent packaging was preferred over active packaging as consumers want to be able to visually monitor product quality themselves using either freshness, microbial growth or toxin risk as well as shelf life conditions such as temperature sensors/indicators (Aday and Yener 2015). The respondents indicated that education through advertising would be the most effective way to increase innovative packaging acceptability. It was noted that increased awareness of innovative packaging in warmer climates such as Italy, Spain and Turkey might be due to their increased concern regarding microbial spoilage.

In a quantitative survey of intelligent food packaging using the intercept method in Beijing, 371 consumers were tested for their acceptance of the new technology (Li et al. 2020). In this study, a high percentage of respondents (81%; $n = 181$) had a qualification in science and technology, although no significant association was measured for education, employment, gender or age. Overall, acceptance of novel packaging was high (56%), with levels increasing when presented with product-specific applications.

A 2020 study of European generation Y respondents ($n = 1249$) used a 7-point scale, where 1 represented “not important” and 7 “very important” to determine the impact of various active and intelligent packaging features” (Tiekstra et al. 2021). Overall, it was clearly determined that packaging was important (score of 5.3) to the consumer with the main properties of protection (6.0), sustainability (5.8), economy, i.e. low cost or good value (5.8), information (5.5), especially to guarantee authenticity and detailed content, convenience (5.2), portability and storage (4.8) and promotion (4.0). Of the intelligent packaging products tested, respondents reported that they would buy packaging that indicated that it had been maintained at the correct temperature (5.9), with a higher response for women (5.9) over men (5.7). This would represent sensors such as the already commercially present freshness indicators and TTIs in Table 3.2. Sensors that showed the ideal consumption temperature, such as CTI's Coors beer label, were the next highest-ranked (5.5) and would include reversible sensors such as the thermochromic devices and inks. Products that brought with it more interaction with the product ranked next in importance (4.7) with a significant preference by women (4.8) over men (4.5) once again. Packaging that provided engagement and leisure (e.g., QR codes, VR and conductive inks) was less appreciated (4.0), while the last appreciated were those that emitted smell (3.8), light or sound (2.7). More than half (51%) of the consumers were willing to pay less than 10% more for intelligent packaging, while almost more a third would pay between 10 and 50% more (28%).

In a 2021 publication, Cammarelle et al. (2021) surveyed 260 Italian consumers using a modified theory of planned behaviour (TPB) model focusing on reducing household food waste. They found that the respondents were more willing to purchase intelligent rather than active packaging. The survey identified the intelligent packaging as freshness indicators (colour change sensors), gas sensors (emitted from the food), leak indicators, temperature indicators (ready to drink/eat) and TTIs. The questionnaire measured several parameters, including attitudes towards food waste, subjective norms, perceived behavioural control, awareness, shopping, planning and leftover reuse routines. The coefficient for willingness to purchase intelligent overactive packaging was higher for all measures aside from the attitude (favourable/unfavourable evaluation of the behaviour), with significant preference of intention to reduce household waste through willingness to purchase intelligent (0.81) overactive packaging (0.68).

The main considerations when developing intelligent packaging and understanding consumer acceptance include improved education and awareness, visual communication of safety authenticity and quality, increased studies specific to individual technologies and food groups, geographical and demographic considerations, and economic and ecological impacts in an atmosphere of openness and trust.

Most of the studies reported were in the form of written or oral questionnaires. Considering non-invasive biometrics, physiological measurement, virtual reality and AI, greater insights into consumer-targeted intelligent packaging could be achieved. Improvements to the application of such technologies could lead to full acceptance of this new and emerging approach to food packaging.

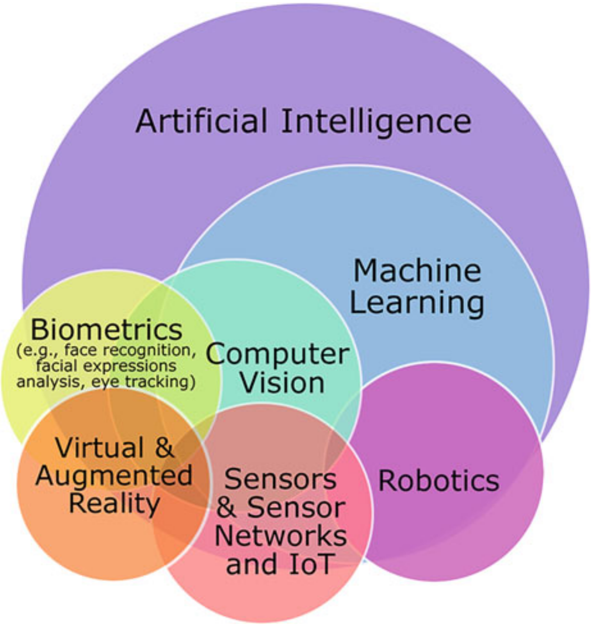

Fig. 3.1 Venn diagram depicting the artificial intelligence sub-disciplines and their relationship within each other. Diagram adapted from Gonzalez Viejo et al. (2019b). IoT: Internet of Things

3.5 Artificial Intelligence in Food Packaging

The implementation of AI has gained increasing popularity in the last decade, especially in the food and beverage sciences (Fuentes et al. 2021a; Gonzalez Viejo et al. 2019b). It is important to note that AI does not involve only machine learning modelling, which is a discipline within AI, but also involve the integration with other disciplines, such as sensor technology, sensor networks and Internet of Things (IoT), robotics, biometrics, VR and AR, computer vision using imaging and multispectral cameras for smart or intelligent assessments (Fig. 3.1).

Different AI modelling strategies have been implemented for food and beverage applications, including packaging assessment, through the use of supervised machine learning and deep learning depending on the data availability and the objectives and targets of the models to be developed (Gonzalez Viejo et al. 2019b). Once the AI models are developed, they can be deployed using the respective sensor technology that is readily available, which can be cost-effective. One of the main principles to consider for efficient AI model deployment is the parsimony requirement of models, which states that the inputs of the models need to be simple enough and easier to acquire compared to the targets (Robbins n.d.).

Recent research is of special relevance, which implemented non-invasive biometrics for emotional and physiological response assessment from panellists in sensory tests. An interesting application of AI was proposed by the Digital Agriculture, Food and Wine research group at the University of Melbourne, using the automated integration of eye trackers and emotional response from participants assessed through computer vision (Fuentes et al. 2019). Through this methodology, it was possible to synchronize the assessment of different components of packaging labels, or AOI and the emotional response elicited by each (Fuentes et al. 2021b). Many other critical applications of AI in the food sector have been identified, such as improvement of quality of packaging and food safety (Paul et al. 2021), and the assessment of coffee labels under social isolation using online video conference resources and computer vision, which makes these studies relevant in times of pandemic (Gonzalez Viejo et al. 2021). Also, data collection and AI modelling have been facilitated recently through the development of a specialized BioSensory App to obtain self-reported data and video and infrared thermal imagery to process them using computer vision algorithms (Fuentes et al. 2018). Although it has not been widely explored, AI may be integrated into intelligent packaging technologies as more efficient anti-counterfeiting strategies. This is a promising application of AI, which is being explored and developed, especially in the most recent years (Schaefer and Cheung 2018). This includes the integration of machine learning to intelligent packaging sensors as support systems for food quality and safety (Sohail et al. 2018). For example, this may predict the product shelf life in real time according to the storage and transportation conditions (Loisel et al. 2021).

3.6 Conclusion

The implementation of new and emerging technologies for intelligent packaging assessment and smart feature integration shows promising results for the food and beverage industries. Implementing AI for packaging assessment of consumer acceptability by integrating sensor technology and machine learning could increase objectivity for the analysis of packaging for new products, which can support the decision-making process more efficiently. More research should focus on the efficient deployment of AI models and sensor integration since most recent developments are only up to the stage of model development. The latter will secure the proper application of AI in smart or intelligent packaging to benefit the industries and consumers through higher information, transparency, provenance, traceability and combat counterfeiting.

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Biodegradable Packaging Materials and Techniques to Improve Their Performance

4

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Abstract

The most used materials for the development of food packaging are petroleum-based polymers. Despite the advantages that synthetic polymers have, the low rates of recycling, coupled with their nonbiodegradability and nonrenewable nature, drive the concerns regarding environmental pollution. Alternatives to replace synthetic polymers include different types of biomolecules, and these molecules might be provided by the metabolism of microorganisms, from biomass, by-products from food industries, and chemical synthesis of bio-derived monomers. Even with many sources being investigated as raw materials for food packaging development, the large use of these bio-based materials is still limited by different reasons. Many strategies can be used to improve the performance of these materials, such as blends, reinforcing agents, cold plasma, UV light, and chemical and enzymatic methods. Thus, an opportunity remains in the search to improve the overall performance of biodegradable materials in order to overcome the limitations regarding their packaging performance for the commercial use.

Keywords

Biopolymers · Bioplastics · Sustainable packaging

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4.1 Introduction

Packaging has a primordial role in the maintenance of the quality of the food products from their production to consumption. The four main functions of food packaging are containment, protection, convenience, and communication. Among the most widely used materials are petroleum-based polymers; however, the wide use of these nonrenewable sources of polymers coupled with the low recycling rates has been causing their accumulation in nature leading to serious environmental problems. In this way, the search for alternatives from renewable and nonpolluting sources is of utmost importance in order to replace these synthetic materials.

The most widely used molecules for the development of sustainable polymers for food packaging materials include polysaccharides, proteins, and lipids. The films developed with macromolecules from agricultural sources have different characteristics regarding their mechanical, color, and barrier properties. Although a wide variety of raw materials have been explored to develop these materials, several factors still limited the advancement of these technologies for commercial use. Among them, the hydrophilic behavior of many proteins and polysaccharides is responsible for the low performance of the developed films compared to the synthetic polymers, avoiding these materials to perform the basic functions of protection of the packaged products (Wihodo and Moraru 2013; Benbettaïeb et al. 2016b).

Polylactic acid (PLA) is a polymer that is characterized as biocompatible and biodegradable thermoplastic aliphatic polyester (Mochizuki 2009), and it is obtained industrially through the polymerization of lactic acid or the polymerization with opening of the lactide ring (Avérous 2008). PLA can be produced from renewable nonfossil natural resources by fermentation of polysaccharides such as sugar or extracted from corn, potatoes, cane molasses, and beets (Murariu and Dubois 2016). One of the major disadvantages of using PLA is its higher cost and deficiency in some properties, such as low thermal resistance and lower barrier properties, limiting its commercial applicability (Swaroop and Shukla 2018).

Polyhydroxyalkanoates (PHAS) are polyesters of natural origin, and these biopolymers are produced by microbial fermentation by a wide variety of bacteria. PHB has thermoplastic properties, which allow them to be molded or transformed into films for different applications. The high crystallinity of polyhydroxybutyrate (PHB) makes the films of these biopolymers very fragile (Ghanbarzadeh and Almasi 2013). Therefore, it is important to search for alternatives to improve the polymer network formed by macromolecules from agricultural sources, microorganisms, and bio-derived monomers.

Different strategies can be used to improve the performance of these materials, such as the mixing of different raw materials to combine their properties, incorporation of reinforcing agents, use of chemical and enzymatic methods for modification of polymer chains, and physical methods that alter the properties of the polymeric networks (Bourtoom 2009). Chemical treatments using acid or alkaline agents or crosslinking agents have shown promising results in relation to mechanical and film barrier performance (Shah et al. 2016; Benbettaïeb et al. 2016b). The use of physical methods such as cold plasma and UV light technologies has the advantages of not requiring chemical reagents, also these techniques are nongeneration waste, and the treatment application has a great uniformity. These technologies are known to alter the properties of polymers by generating radicals that initiate reactions in their structure, such as the formation of crosslinking, and/or the breaking and degradation of chains (etching) (Morent et al. 2011; Wihodo and Moraru 2013). Due to these characteristics, the study of cold plasma and UV light to modify the properties of films developed with molecules from agricultural sources is promising since they are nonpolluting technologies being used for the improvement of polymers from renewable sources.

This chapter aims to present a review of biodegradable polymers used in the development of food packaging, as well as the techniques that can improve the performance of these biodegradable materials in relation to physical, mechanical, and barrier properties.

4.2 Biopolymers

In view of the environmental impacts generated by the disposal of the use of nonbiodegradable packaging, the search for alternative materials for the production of biodegradable packaging is necessary and has been intensified and the latest years (Cazón et al. 2017; Thakur et al. 2018). In this context, biodegradable and/or bio-based polymers, also called biopolymers, are alternative sources that have been widely studied for this replacement since they are raw materials with the ability to decompose in nature in a short period of time after disuse (Gouveia et al. 2019; Nešić et al. 2020). Biopolymers are polymers obtained from natural sources, which can be extracted from plants or marine organisms, such as polysaccharides and proteins, or produced by microorganisms (Paixão et al. 2019), such as microbial polyesters (PHAs) or microbial polysaccharides (Nešić et al. 2020), and also could be chemically synthesized from biological material (Rogovina et al. 2019). Figure 4.1 shows the most used sources of biopolymers for food packaging production.

It is worth noting that in order to obtain biopolymeric films of proteins and polysaccharides, in most cases it is necessary to incorporate plasticizer additives to modify and improve properties, since the use of polymer alone is not sufficient to form rigid or elastic films with good barrier properties (Han 2014). Reinforcement materials such as composite materials or bioactive compounds can also improve the physical–chemical properties of the polymeric matrix (Zafar et al. 2016; Kumar et al. 2019).

The addition of plasticizer has the function of reducing the strain stress and hardness and increase the flexibility and resistance to fracture the biopolymeric films. However, the modification of the properties will be related to the combination of the polymer and the plasticizer used (Vieira et al. 2011; Espitia et al. 2014). According to Espitia et al. (2014), among the most used plasticizers are polyols (glycerol and sorbitol), lipids (monoglycerides, phospholipids, and surfactants), and sugars (glucose and sucrose).

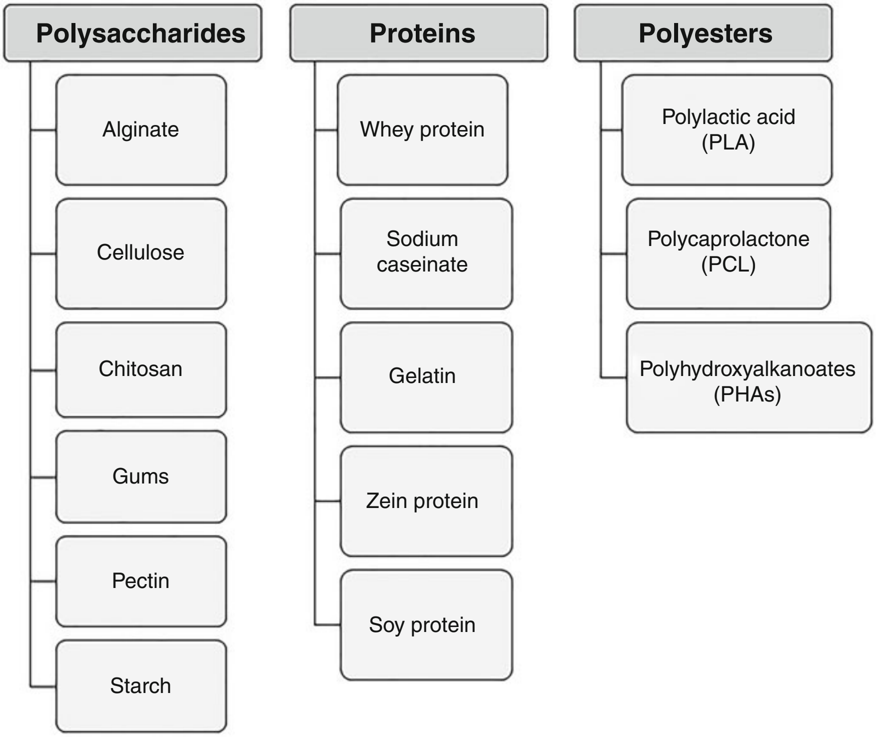

Fig. 4.1 Types of biopolymers used for the preparation of food packaging

4.2.1 Polysaccharide-Based Films

Polysaccharides are promising sources for the development of packaging for food products, since they are a group of polymeric carbohydrates with desirable characteristics such as biocompatibility, biodegradability, and nontoxicity to live organisms (Chopin et al. 2014; Nešić et al. 2020). This biopolymer is a very abundant raw material, which could be originated from plants and marine biomass (Cazón et al. 2017; Nešić et al. 2020), bacteria, or fungi (Delattre et al. 2007).

In general, polysaccharide-based films have low barrier properties to water vapor and poor mechanical stability, due to the hydrophilic nature of most of these polymers (Cazón et al. 2017) However, polysaccharide packaging has good barrier properties to oxygen and carbon dioxide when exposed to low or moderate relative humidity (Nešić et al. 2020). The packages can be directed to products compatible with their properties; for example, some polysaccharides, e.g., alginate and carrageenan, are hydrophilic and hygroscopic and can be applied on the food surface to absorb water and slowing the loss of moisture (Bourtoom 2008; Cazón et al. 2017). Although there are some limitations for the preparation of biodegradable packaging, it is possible to improve the natural properties of polysaccharides through chemical modifications, in order to obtain molecular structures of interest and functionalized (Majid et al. 2018) The desired properties in polysaccharide films can also be obtained by combining them with other polymers and incorporating nanocomposites and/or bioactive compounds in the system (Hussain et al. 2017; Nešić et al. 2020).

Among the most used polysaccharides for the development of films are alginate, starch, cellulose, gums, pectin, and chitosan. In the next topic, the sources, desirable and undesirable characteristics, and some studies using different polysaccharides in the development of food packaging will be addressed.

4.2.1.1 Alginate

Alginate is a polysaccharide obtained from the alkaline treatment of alginic acid, extracted from cell walls of brown seaweed (*Phaeophyceae*), also can be obtained from bacterial sources (Aziz et al. 2018). The algae species most used for alginate extraction are *Ascophyllum nodosum, Fucus* species, *Laminaria* species, *Macrocystis pyrifera,* and *Ecklonia* (Hay et al. 2013; SenturkParreidt et al. 2018). On the other hand, the extraction from a bacterial source occurs through the species of *Pseudomonas* and *Azotobacter* (Hay et al. 2013).

Due to the high hygroscopic, water-soluble properties, ease gel formation at room temperature, and emulsification capacity, alginate has shown great potential for the production of biodegradable films (Fig. 4.2). The films produced with alginate presented low permeability to oil and oxygen, in addition to having good flexibility, gloss, and absence of flavor and odor (Pawar and Edgar 2011; Paixão et al. 2019). According to Cazón et al. (2017), alginate films offer a low moisture barrier, and their hygroscopicity makes possible a delay dehydration of the foods in which they are applied. However, it can be used to mix polymers to get films with higher barrier properties, and despite the characteristics, alginate salts can also be modified by the process of crosslinking and/or adding lipids in the formulation, thus increasing the barrier to humidity (Benavides et al. 2012; SenturkParreidt et al. 2018).

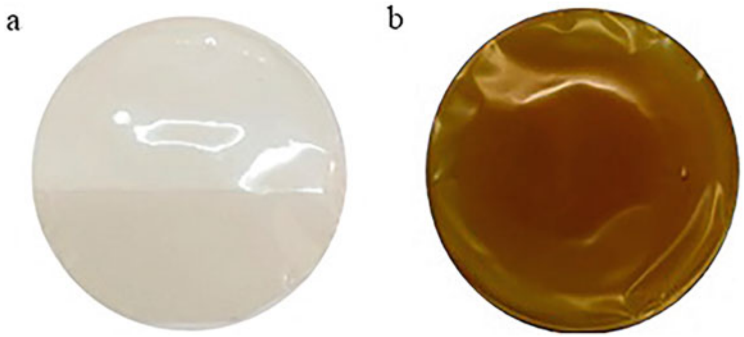

Fig. 4.2 Sodium alginate-based films (**a**) and alginate based-film incorporated with *Caryocarbrasiliense* extract (**b**)

4.2.1.2 Cellulose

Cellulose is the most abundant biopolymer in the world, being present mainly in plants due to cell development and biogenesis of cellulose in vegetables (Moon et al. 2011). However, this biopolymer can be found in fungi, algae, marine organisms, invertebrates, and gram-negative bacteria (Jõgi and Bhat 2020). It is one of the first biopolymers to be applied in the development of biodegradable packaging. Many packaging based on cellulose is used, as paper, cardboard box, wood box, among others.

A single cellulose fiber has Young's modulus values above 114 GPa, crystallinity about 89%, and a high degree of polymerization, with a thermal degradation temperature above 230 °C (Srivastava et al. 2018). Cellulose is commonly used in the paper and textile industries, generating materials of high quality and resistance, being applied as coatings and multilayer packaging for various types of food. However, due to the hydrophilic character, low solubility, and high crystallinity, the formation of films based on native cellulose becomes unfeasible because of the difficulty of the process and its high costs (Nechita and Iana-Roman 2020). Therefore, cellulose derivatives such as carboxymethylcellulose (CMC), methylcellulose (MC), ethyl cellulose (EC), hydroxypropyl and hydroxyethyl cellulose (HPC and HEC), and hydroxypropyl methylcellulose (HPMC) could be used to produce biodegradable films and membranes (Thakur and Thakur 2016).

In addition, due to the previously mentioned properties of high strength, crystallinity, and biodegradability, cellulose fibers can be reduced to nanocellulose (by mechanical or acid hydrolysis method) and applied as nanocomposites in the development of food packaging (Vestena et al. 2016; Hafemann et al. 2019). The incorporation of nanocellulose particles in filmogenic solutions can promote good emulsion and viscosity characteristics of fluids and, due to the hydroxyl groups present, nanoparticles can assist in the interaction between polymeric networks and lipophilic compounds, promoting the development of films more homogeneous and with greater resistance, malleability, and desirable barriers to UV light and gases (Mu et al. 2019).

4.2.1.3 Chitosan

Chitosan is a copolymer, obtained from the deacetylation of chitin (Brasselet et al. 2019). Chitin is a naturally occurring polysaccharide that is among one of the most abundant biopolymers; however, its application is limited because it is not soluble in water or other common organic solvents, requiring its alkaline deacetylation in a solid state, which can also be obtained by fermentation (Jayakumar et al. 2010). After deacetylation, chitosan is obtained, and this polysaccharide is composed of two different monomers N-acetylglucosamine and glucosamine linked by β-(1 → 4)–glycosidic bonds (Younes and Rinaudo 2015).

According to Fernandez-Saiz (2011), chitosan is a polymer that presents bioavailability, biocompatibility, bio-adhesiveness, and biodegradability, is nontoxic, and can be ingested, in addition to intrinsic antimicrobial properties against fungi and bacteria (Laroche et al. 2018; Brasselet et al. 2019). Due to the physical and chemical properties of chitosan, several studies have demonstrated the potential of this biopolymer for the development of food packaging (Souza et al. 2017, 2019; Nešić et al. 2020). In films, chitosan has selective permeability to gases such as O_2 and CO_2 and good mechanical properties. However, the chitosan presents a poor water barrier due to its high sensitivity to water (Fernandez-Saiz 2011; Priyadarshi et al. 2018; Bouissil et al. 2019).

More recent studies have explored the development of active packaging using chitosan-based films incorporated with antioxidant and antimicrobial compounds as a strategy to improve the properties of chitosan films (Souza et al. 2017; Nešić et al. 2020). Bonilla et al. (2018), analyzing chitosan films (C) incorporated with clove oil (CO) and ginger oil (GO), observed that the incorporation of essential oil produced films with greater antioxidant activity, being CO > GO > C. Both films incorporated with essential oil showed better UV-Vis light barrier properties. The addition of clove oil also increased the properties of tensile strength and elastic modulus, compared to pure chitosan, showing that essential oils not only function as a bioactive compound, but also function as a reinforcing agent.

Studies also show that chitosan can be applied in the production of intelligent packaging, taking as an example the study of Wu et al. (2019), which used chitosan for the elaboration of intelligent packaging based on the incorporation of anthocyanins extracted from black rice bran, in which the response was characterized by pH sensitivity, higher antioxidant properties, and UV barrier effect.

Chitosan films can be applied to different products, as fruits, cuts of meat, biscuits, and butter (Drevinskas et al. 2017; Mostafavi and Zaeim 2020). In meat products, can be cited the study of Ruiz-Navajas et al. (2015), where chitosan films incorporated with nanocomposites of montmorillonite and rosemary essential oil were able to reduce the oxidation and color change of chicken meat.

4.2.1.4 Gums

According to Salehi and Kashaninejad (2015), the term "gum" is applied to refer to a group of naturally occurring polysaccharides that have the capacity to form gels, viscous solutions, or emulsion stabilizers, also can be used as texture modifiers, thickeners, gelling agents, dietary fiber, and on the development of films and coatings (Kurt and Kahyaoglu 2014; Dick et al. 2015). Another nomenclature used is "hydrocolloids," referring to water-soluble gums (Salehi and Kashaninejad 2015). In general, the gums can be defined as molecules of high molecular weight that can produce gel when combined with appropriate solvents (Quiroga 2015).

The gums can be extracted from terrestrial or marine vegetables, products of microorganism biosynthesis, and chemical modification of natural polysaccharides (Quiroga 2015). Several studies have demonstrated the potential of the application of gums in the development of biodegradable food packaging, and some of them are shown in Table 4.1.

Among the polysaccharides capable of forming films, the gums are the class of mannans (consisting of glucomannan), present high molecular weight polymers, and have a strong interaction with water (Kurt and Kahyaoglu 2014).

Several studies have used agar as a raw material to produce films (Abdul Khalil et al. 2017; Contardi et al. 2019; Xu et al. 2019). In general, agar-based films are

Table 4.1 List of gums more common used in the films production

Gums	Source	References
Agar	Red seaweed of the class *Rhodophyceae* (*Gelidium* sp. and *Gracilaria* sp.)	Mostafavi and Zaeim (2020); Sousa and Gonçalves (2015)
Arabic	Exudate from Acacia Senegal and other species of the family *Leguminosae.*	Murmu and Mishra (2018); Murmu and Mishra (2017)
Carrageenan	Red seaweed of theRhodophyceae family: *Chondrus crispus* and *Gigantinamamillosa*	Rhim and Wang (2014); Siah et al. (2015); Sedayu et al. (2019)
Gellan	Secreted by the bacteria *Sphingomonas elodea*	Kim et al. (2015); Sapper et al. (2018)
Guar	*Cyamopsis tetragonolobus* seeds	Saurabh et al. (2015); Liu et al. (2020)
Locust	Ceratonia siliquo of the family *Leguminosae*	Barak and Mudgil (2014); Liu et al. (2020)
Unconventional	Chia seed	Barak and Mudgil (2014); Dick et al. (2015)
	Salep glucomannan of roots or tubers	Kurt and Kahyaoglu (2014)
	Basil seed (*OcimumbasilicumL.*)	Khazaei et al. (2014)

relatively brittle, showing low elasticity and thermal stability, high solubility, and water vapor permeability (Arham et al. 2016). On the other hand, agar films have a high rate of shrinkage, are transparent, and heat-sealable, as well as biodegradable. However, worth to remember the film formation capacity of the agar is based on the gelling property and is closely linked to the origin of the source, the method of production of the film, and the components incorporated in the matrix (Sousa and Gonçalves 2015; Garrido et al. 2016; Huang et al. 2020).

Agar and carrageen are natural hydrophilic polymers extracted from red algae (Gonsalves et al. 2011; Siah et al. 2015), and films obtained from these polymers have limited use because it is a highly hydrophilic compound, but have a good barrier for fats and oils (Tavassoli-Kafrani et al. 2016). Capable of forming highly viscous solutions even at low levels of concentration, the xanthan gum has an excellent ability to form films (Mohsin et al. 2018; Murmu and Mishra 2018). However, the xanthan films also have poor mechanical properties (Kurt et al. 2017; Hao et al. 2018; Wu et al. 2018b). As well as other polysaccharides, the properties of these polymers can be improved by mixing other polymers (Hou et al. 2019) or by incorporation of bioactive compounds (Rhim and Wang 2014; Soni et al. 2016).

Cashew bark is a nonconventional gum source, and it is a nonallergenic, biocompatible, and biodegradable polymer obtained from the gummy exudate extracted from *Anacardium occidentale* (Nayak et al. n.d.). Films made only of cashew gum have poor mechanical properties and low stability; for this reason, some studies have analyzed the mixture of polymers with this matrix (Oliveira et al. 2018; Cruz et al. 2019).

Another nonconventional gum is the gum obtained from chia seeds, and the mucilage extracted from chia has the potential to produce edible films (Muñoz et al. 2012; Barak and Mudgil 2014), coatings (Dick et al. 2015), and soluble films (Fernandes et al. 2020). The mucilage is mainly composed of xylose, glucose, and methyl glucuronic acid that form a branched polysaccharide of high molecular weight with excellent gelling properties in aqueous solution, even in very low concentrations (Barak and Mudgil 2014).

Other sources are studied in order to evaluate the potential for the elaboration of biopolymeric packaging, such as *salep glucomannan* extracted from tuberculosis roots (Kurt and Kahyaoglu 2014), basil (*Ocimum basilicum L.*) seed gum (Khazaei et al. 2014), *Lepidium perfoliatum* seed gum (Seyedi et al. 2014), Brea gum extracted from *Circadian praecox* (Spotti et al. 2016), and tara gum (Wu et al. 2018b; Liu et al. 2020).

4.2.1.5 Pectin

Pectin is one of the main structural polysaccharides of superior plant cells, and pectin is found mainly in citrus fruits and apples, and can also be extracted from by-products of the food industry, such as fruit and greenery marcs. It is an important biopolymer in the food industry due to its gelling properties, generally formed by water-soluble pectinic acids with varying levels of ester methyl, with the ability to form gels when combined with sugars and acids in appropriate proportions (Narasimman and Sethuraman 2016; Martău et al. 2019; Coman et al. 2020).

Chemically, pectin is constituted by poly α1–4-galacturonic acids, can be classified according to its degree of esterification with methanol as high methoxy pectin (DE $<50\%$) or low methoxy pectin (DE $>50\%$) (Espitia et al. 2014). However, the source and conditions of extraction can affect the molecular weight of the pectin and the degree of esterification (DE) (Gouveia et al. 2019).

In the food industries, pectin is applied mainly as a stabilizer, thickener, and encapsulant (Rodriguez-Garcia et al. 2016). However, it is widely studied in different fields such as agriculture and medicine (Gupta et al. 2014; Smith et al. 2016). In addition to the ability to form gels, pectin has antimicrobial and antiviral properties, which can be directed toward the development of active films and coatings (Gouveia et al. 2019).

Generally, pectin films are produced by casting technique (Bátori et al. 2017), but other methods such as thermocompression or extrusion have been studied due to their simplicity and their ability to produce films without polymer solubilization (Gouveia et al. 2019).

Pectin films have high-water solubility and poor mechanical properties, limiting their application as food packaging (Nesic and Seslija 2017; Gouveia et al. 2019). In order to improve these properties Makaremi et al. (2019) incorporated clay nanoparticles into a pectin matrix, obtaining pectin films with better mechanical performance, thermal stability and water vapor barrier properties.

Another strategy to improve the properties of pectin films is the incorporation of polyols. In the study made by Norcino et al. (2020), biodegradable pectin films were elaborated with incorporation of copaiba oil nanoemulsions in order to study the interactions of the polymers and how they influenced the mechanical and morphological properties of the films. It was observed that the incorporation of copaiba oil resulted in a gradual decrease in the modulus of elasticity and tensile strength, while increasing elongation art break, it was also observed an inhibition of microbial growth after the addition of copaiba oil, thus obtaining active packaging.

4.2.1.6 Starch

Starch is a polymer with great potential for manufacturing biodegradable packaging because it is a low cost and could be obtained from different plant sources (Dai et al. 2019). However, the properties of starch films are dependent on the source of the polysaccharide, and they are commonly extracted from rice, potatoes, cassava (Luchese et al. 2017b), corn, and wheat (Luchese et al. 2018; Sivakanthan et al. 2020). However, alternative sources for obtaining starch are studied, such as lentils, beans (Joshi et al. 2013), peas, jackfruit, mango, and yams (Li et al. 2019; Rodrigues et al. 2020).

Chemically, starch consists of a crystalline linear amylose polymer (poly-α-1,4-D-glucopyranoside) and highly branched amylopectin formed by a large number of D-glucose units linked by α-1,4 and α-1,6-glycoside bonds (Sivakanthan et al. 2020). When starch is solubilized in an aqueous solution, and subsequently heated to a certain temperature, the starch granules absorb a large amount of water, and swell or even collapse, releasing the amylose, occurring the process of gelatinization and increased viscosity of the solution, which is used in the development of edible coatings and biodegradable films (Dai et al. 2019; Li et al. 2019; Ruan et al. 2019).

In general, starch-based films are great alternatives for food packaging due to the transparent, tasteless, and odorless, being materials with good oxygen barrier properties (Sapper et al. 2018). On the other hand, starch film has limited use, due to the high sensitivity to water and retrogradation phenomena that influence the barrier and mechanical properties of these materials (Cano et al. 2014; Kumar et al. 2019).

Although the limitations inherent starch films, the properties can be improved through physical and chemical modifications of the polymer matrix (Nechita and Iana-Roman 2020). The starch modification consists of the alteration of the native characteristics of the starch by the introduction of new functional groups in the molecules of the polysaccharide, changing the molecular size of the polymer and the properties of the particles (Liu et al. 2018; Kumar et al. 2019). Physical modification generally consists of combinations of polymeric matrix or addition of nanoparticles (Kumar et al. 2019), while chemical modification consists of structural modification as the crosslinking process.

In the study of Dai et al. (2019) was evaluated the physicochemical properties of native cassava starch and films of cassava starch modified by different methods. It has been observed that modified starches have better properties than native starch. When comparing the modification methods, they observed that the starch modified by crosslinking had better mechanical properties and water vapor barrier in relation to the esterified starch and the oxidized starch.

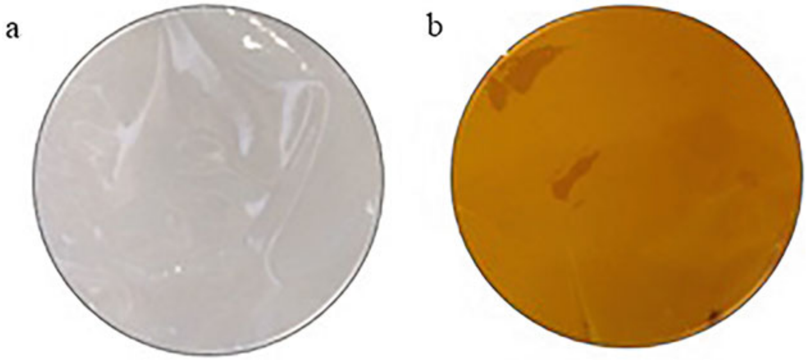

Fig. 4.3 Cassava starch films plasticized with glycerol (**a**) and active cassava starch-based film incorporated with Annatto extract (*Bixa orellana*) (**b**)

Luchese et al. (2018) evaluated the properties of films made with different conventional sources of starch (wheat, potatoes, cassava, and corn), and it was observed that cassava starch presented more hydrophobic surfaces than corn and wheat starch films. Higher water vapor permeability values and lower mechanical properties values were also found for wheat starch films. While films of cassava starch showed higher values of elongation at break and lower permeability to water vapor.

Acosta et al. (2015) propose mixing starch with other biopolymers to improve the physical and functional properties of films, in addition to the incorporation of hydrophobic substances or antimicrobial compounds to produce active films (Fig. 4.3). Evangelho et al. (2019) incorporated orange essential oil in corn starch. The films incorporated with essential oil showed greater antibacterial activity against *Staphylococcus aureus* and *Listeria monocytogenes*, obtaining active packaging. The addition of oil also influenced the properties of the films, causing a reduction in tensile strength and elongation, increasing the moisture content, water solubility, and water vapor permeability.

Menzel et al. (2019) evaluated potato starch films incorporated with sunflower peel extract for preparation of active packaging. The addition of sunflower peel extract proved to be a valuable source of a natural antioxidant extract, and the incorporation of up to 6% of active compounds altered the mechanical properties, generating less elastic module and more durable films, and attributing this alteration mainly to the interactions of the phenolic compounds of the extracts with the polymeric starch network.

In general, it was observed that several sources of starches have potential for the development of biodegradable packaging; however, many of these matrices require chemical and or physical modifications to obtain packaging with more applicable properties.

4.3 Protein-Based Films

Proteins are among the most used natural biopolymers to produce films, and it is due to the presence of several polar and nonpolar amino acids that confer specific structural and functional variations (Scudeler et al. 2020). Proteins are heteropolymer composed of more than one hundred amino acids (monomers) linked through peptide bonds. Each of these amino acids contains a central carbon linked to a carboxyl group, a hydrogen, an amino group, and a R group (Nur Hanani et al. 2014).

When applied to packaging development, proteins have promising properties due to their ability to form three-dimensional networks stabilized and strengthened by hydrogen bonds, hydrophobic interactions, and disulfide bonds, allowing the creation of intermolecular bonds and cohesive matrices (Benbettaïeb et al. 2016a). However, the hydrophilic nature of proteins affects mechanical and barrier performance, which are essential properties for food packaging materials (Benbettaïeb et al. 2016c).

Protein biopolymers from animal and vegetable origin are of great interest for film production due to their relatively low cost, inherent biodegradability, and high availability as by-products from food and agriculture industries (Janjarasskul and Krochta 2010; Reddy and Yang 2013). Another advantage is that protein polymers can be processed by various methods, such as solvent evaporation or thermomechanical processes to produce films, developing materials with excellent oxygen barrier properties and adequate mechanical properties (Guerrero et al. 2010; Song et al. 2011).

There are several sources of proteins that have the ability to produce films. Some of them are whey proteins, sodium caseinate, gelatin (bovine, swine, and fish), corn, and soy proteins (Huntrakul et al. 2020).

4.3.1 Whey Protein

Whey proteins have been of great interest; currently, the world production of whey is about 1.8–1.9 × 10^8 tons/year. Whey proteins are responsible for 20% of the total milk protein, being a co-product of cheese production, and it is recovered through ultrafiltration or diafiltration. The main constituents of whey protein are α-lactalbumin, β-lactoglobulin, immunoglobulin, and bovine serum albumin (Smithers 2008; Tsai and Weng 2019).

According to Zhang et al. (2020b), whey proteins include whey protein isolate (WPI), whey protein concentrate (WPC), and whey protein hydrolysates. WPI has values above 90% of protein, and the main components are α-lactalbumin and β-lactoglobulin. The whey protein concentrate (WPC) is separated from the whey by ultrafiltration, and has strong nutritional properties and film formation capacity, which is transparent and elastic, making it a biodegradable and renewable source of protein of high biological value (Smithers 2008).

Protein-based films have no aroma and flavor and present good transparency, allowing a wide range of applications. Despite the promising use for packaging, the films produced have moderate mechanical characteristics, but poor water resistance due to their hydrophilic fractions. The high-water vapor permeability limits their application as packaging material when compared to synthetic polymers (Oymaci and Altinkaya 2016; Yayli et al. 2017).

GökkayaErdem et al. 2019 investigated the effect of the addition of sunflower oil on the formation of edible biocomposite films based on whey protein. The authors found that the water vapor permeability values decreased regardless of the added oil concentration, and their barrier properties were improved. Janjarasskul et al. (2020) developed edible films, based on whey protein (WPI) to package food or dry ingredients. The authors report that the films showed good permeability to water vapor and oxygen and low values for the mechanical properties of tensile strength, elongation, and modulus of elasticity and concluded that the films have the potential to be used as leave-in packaging for food dried in portions.

Zhang et al. (2020b) produced films composed of isolated whey protein (WPI) and psyllium seed gum (PSG), and the authors note that the WPI/PSG composite films had a greater contact angle with water and vapor permeability of water, demonstrating greater hydrophobicity, as well as less oxygen permeability and light transmittance compared to individual WPI or PSG films. It was also observed that the tensile strength, elongation at break, and the modulus of elasticity of the composite film WPI/PSG were higher than in the individual films.

4.3.2 Sodium Caseinate

Sodium caseinate is a mixture of casein monomers and small aggregates formed after elimination of colloidal calcium phosphate from casein micelles (Pankaj et al. 2014a). The technical and functional properties of caseinates make them proteins used mainly to improve the emulsifying properties of food matrices and the development of edible films (Broyard and Gaucheron 2015).

Due to the high proportion of polar groups, sodium caseinate films are good barriers to nonpolar substances, such as oxygen, carbon dioxide, and aromatic compounds. On the other hand, they present low resistance to traction and do not present a good barrier to water vapor due to their relatively high hydrophilicity (Belyamani et al. 2014; Jiang et al. 2020; Lin et al. 2020). Different types of physical, chemical, and biochemical modifications can be used to improve the structure and functionality of caseinates (Broyard and Gaucheron 2015; Picchio et al. 2018).

Brzoska et al. (2018) studied the effects of plasticizers sorbitol and glycerol and the concentration of lipids (oleic acid or mixtures of oleic acid–beeswax) in films based on sodium caseinate. According to the authors, films plasticized with sorbitol were more rigid than those with glycerol and it was also possible to observe a decline in the rate of moisture transmission with the addition of 10% bee wax.

4.3.3 Gelatin

Gelatin is a biodegradable and renewable material, obtained by the chemical or thermal degradation of collagen, and is widely found in skin, bones, and connective tissue (Chiellini et al. 2001; Rbini et al. 2020). In addition, skin, bone, or animal tissues constitute a significant by-product from animal processing industry, generating waste and pollution problems, and these by-products are capable of providing a valuable source of gelatin (Badii and Howell 2006).

Gelatin presents a unique sequence of amino acids with high content of glycine, proline, and hydroxyproline. The content of proline and hydroxyproline is particularly important in terms of the gelling effect (Gomez-Guillen et al. 2011). It is a material of relatively low cost and easy to obtain, being widely used by the food, cosmetic, and pharmaceutical industries due to its functional and technological properties (Badii and Howell 2006).

Its characteristics of biocompatibility, high availability, good processability, biodegradability, low cost, and absence of toxicity make gelatin a suitable material for the production of food packaging (Badhe et al. 2017; Hosseini and Gómez-Guillén 2018; Rbini et al. 2020). As one of the potential biomolecules for film development, gelatin has been extensively studied due to its good film-forming properties and its application as an encapsulating material, as well as a carrier of active ingredients (Gómez-Guillén et al. 2009; Shankar et al. 2017).

The films made with gelatin have good oxygen barrier properties. On the other hand, it has moderate mechanical properties, and relatively poor thermal stability (Gómez-Guillén et al. 2009; Wang et al. 2014) and its high-water permeability limit its industrial applications. However, gelatin functionality can be improved by mixing with other ingredients, such as plasticizers and food additives. The use of plasticizers improves the stability, resistance, and flexibility in gelatin films, which allows its use as packaging material (Park et al. 2008).

Nur Hanani et al. 2012 produced films with bovine, swine, and fish gelatin in different concentrations. The authors observed that films with a higher concentration of gelatin had their mechanical properties improved. Fish gelatin films showed the lowest water vapor permeability values, while films derived from swine gelatin showed less water solubility compared to those formed with fish and bovine skin, regardless of the concentrations used.

In the study of Dammak et al. (2017), an active gelatin-based film was developed, and microparticles coated with chitosan were prepared to encapsulate the rutin. The authors comment that results for water vapor permeability and the mechanical properties of tensile strength, elongation, and modulus of elasticity showed a decrease in values when the concentration of chitosan was greater than 0.5%. The microstructure analysis of the films revealed different micropores soaked in oil, resulting from the incorporation of the microparticles in the gelatin matrix, and they concluded that the film can be a good alternative to incorporate fat-soluble active compounds to design an active packaging.

Khedri et al. (2021) investigate the effects of bioactive casein phosphopeptides (CPPS) on gelatin-based films and reported that the addition of CPPs to the films significantly decreased solubility and water vapor permeability. The films also showed improved mechanical properties when compared to the standard and the FTIR and DSC analyses indicated adequate interactions between the functional groups of gelatins and CPPS.

4.3.3.1 Fish Gelatin

Gelatin prepared from fish skin has advantages over bovine and swine, such as the deficit in outbreaks of bovine spongiform encephalopathy (BSE) and religious restrictions (Islam and Judaism) (Rattaya et al. 2009; Kwak et al. 2017). Fish-derived gelatin (FG) is known to have a relatively low amino acid content (hydroxyproline and proline) compared to mammalian gelatin, presenting less strength in the formation of gels and, therefore, are more suitable for application in films (Karim and Bhat 2009).

Fish gelatin films exhibit good physical and mechanical properties and have an oxygen barrier superior to synthetic films (Nilsuwan et al. 2017). However, they have disadvantages such as high-water solubility and low-water barrier property, due to its high hydrophilicity (Vanin et al. 2005). One way to improve the mechanical properties and moisture susceptibility of films is to modify the polymer network by inducing intermolecular and intramolecular chemical bonds through chemical, enzymatic, or physical treatment (Kwak et al. 2017).

Syahida et al. (2020) studied fish gelatin films added with different concentrations of palm wax (PW) (0–60%). The results showed that gelatin/palm wax films with a higher concentration of PW were thicker, opaque, and more flexible than the control films without PW. The tensile strength increased with the incorporation of 15% PW and also showed a lower water vapor permeability and greater contact angle than the control film.

4.3.4 Fish Protein

Proteins attract attention due to their structure, which has the ability to form strong three-dimensional networks (Rhim et al. 2013; Benbettaïeb et al. 2016a). Animal proteins, such as myofibrillar proteins, are more promising due to their ability to form slightly transparent films with excellent barrier properties to ultraviolet light compared to commercial polyvinyl chloride film, for example (Kaewprachu et al. 2016, 2017).

Fish myofibrillar proteins (FMPs) have become a resource that they can be used to produce films with good transparency and resistance. These proteins are completely filamentous and elastic, and play a functional role because they have functional groups to form intra- and intermolecular bonds in the food system (Limpan et al. 2012; Blanco-Pascual et al. 2014). The use of fish myofibrillar proteins is also taken into account due to the economic aspects and the need to find adequate ways to take advantage of the remaining residues and by-products of fish production and processing (Hamaguchi et al. 2007; Pires et al. 2013).

Myofibrillar proteins extracted from the muscles of several species of fish have been used successfully for film production. In general, films have poor mechanical properties compared to synthetic polymers. Shabanpour et al. (2018) produced films of fish myofibrillar proteins adding bacterial cellulose nanofibers. The authors report that the addition of nanofibers led to a 49% increase in tensile strength, as well as a reduction in water vapor permeability, swelling, and solubility properties, and the evaluation of the thermal properties of these films suggests an improvement in the thermal stability of them.

The search for alternatives to improve the properties of materials of biological origin is necessary to make them suitable for use in food packaging without compromising the food product quality. Strategies to improve the performance of these bio-based polymers, such as the use of chemicals (López De Dicastillo et al. 2016), enzymes (Al-Hassan and Norziah 2017; Kaewprachu et al. 2017), mixed with other materials (Mujtaba et al. 2017; Romani et al. 2019), and others, have been widely studied, and physical strategies, such as cold plasma, are ecological and dry processes and its use can be explored.

Romani et al. (2019) investigated the use of cold plasma as a surface modification strategy for the treatment of films prepared from fish myofibrillar proteins (Fig. 4.4). The authors point out that films treated for 2 min with cold plasma showed an increase in elongation at break and a decrease in tensile strength. However, the plasma treatment could be a promising alternative in order to improve the properties of myofibrillar protein films for food packaging.

Fig. 4.4 Fish myofibrillar protein film (Source: Romani et al. (2019))

4.3.5 Corn Protein Films

Zein is a prolamin polymer derived from corn, which is a co-product obtained during the extraction of corn starch (Ghanbarzadeh et al. 2006). The zein is insoluble in water, and this characteristic occurs due to the low content of polar amino acids and the high content of nonpolar amino acids present in the structure (Yong Cho et al. 2002).

Many studies in the pharmaceutical and food areas illustrate the potential of zein as a material for packaging production due to its biocompatibility, biodegradability, and nontoxicity (Han et al. 2014; Paliwal and Palakurthi 2014; Wang et al. 2019), in addition to its ability to incorporate bioactive compounds (Ozcalik and Tihminlioglu 2013; Yin et al. 2014; Wang et al. 2019). With the composition of 1/4 of the hydrophilic amino acid residues and 3/4 of the lipophilic amino acids, zein has inherent hydrophobic properties (Sun et al. 2017).

The development of methods to improve the functional properties of zein films, especially the mechanical properties and wettability, present challenges for their applications, such as increasing the shelf life of food products, tissue engineering, grafting, or printing of materials (Wang et al. 2009; Paliwal and Palakurthi 2014). Kadam et al. (2017) evaluated the effect of adding TiO_2 nanoparticles on the thermomechanical properties of zein films, where they observed that the incorporation of nanoparticles changed the properties of the films and improved some of their mechanical properties; however, it reduced the elongation at break in 50%.

The study of Gu et al. (2013) sought to improve the flexibility of zein films by adding gliadin. The authors report that there was a significant improvement in the flexibility of the films, as the amount of gliadin added to the solution increased, the water vapor permeability decreased. Indicating that the interactions of zein and gliadin established a solid network structure, gliadin conferred extensibility, and zein contributed to the resistance of the films.

Nogueira and Martins et al. (2018) developed and characterized zein/hake protein isolate (*Cynoscion guatacupa*) bilayer films (Fig. 4.5). The authors comment that the bilayer film was malleable and easy to handle, and with improved mechanical and thermal properties, they also report that the structural assessment of the bilayer revealed interaction between the different polymer layers and it was not necessary to use any type of adhesive to form a single structure.

4.3.6 Soy Protein Films

One of the most important by-products of the soy oil industry is the soy protein isolate (SPI), but its economic value is lower compared to the lipid components (Siracusa 2012; Koshy et al. 2015). SPI contains a large number of polar amino acids that provide hydrophilicity to SPI-based materials, and this effect is reflected in the film's fragility against moisture, resulting in a poor water vapor barrier and

Fig. 4.5 Bilayer film of isolated protein from hake and zein (Source: Nogueira and Martins et al. (2018))

insufficient mechanical properties when compared to some synthetics films (González et al. 2011).

Wang et al. (2016) developed antioxidant films of isolated soy protein with aqueous extract of Chinese chestnut (*Castanea molíssima*). The authors report that the films presented a good barrier to ultraviolet light and oxygen and the hydrophilic properties were improved. Advances in research involving the protein polymer have been recognized, but further studies are needed. Then, more alternatives can be presented to improve the physical and mechanical properties of the protein's films in general.

4.4 Biopolymers Produced by Biotechnological Processes

An alternative for obtaining biodegradable polymers is through biotechnological processes, using enzymes, fungi, and bacteria. The most well known are polylactic acid, polyhydroxyalkanoates, and polyhydroxybutyrate, which have great diffusion and industrial application in the development of commercial biodegradable packaging (Jõgi and Bhat 2020). These biopolymers and their derivatives have characteristics and properties similar to conventional petroleum-based polymers, and among the types of biopolymers presented above, polyesters have greater industrial application in replacing conventional packaging.

4.4.1 Polylactic Acid (PLA)

PLA aliphatic polyester is a bio-based polymer produced industrially, being applied in the development of packaging for food and medical materials due to its characteristics of thermoplasticity, transparency, biodegradability, and biocompatibility (Nofar et al. 2019). Discovered in 1845, PLA is produced from the chemical synthesis of lactic acid obtained from bacterial glucose fermentation, which can be derived from corn starch, sugar beet, sugar cane, and other renewable biomass and waste (Srivastava et al. 2018).

Initially, new polymerization techniques were studied to obtain PLA with high molecular weight (higher than 100.000 g/mol), which offer better physical and mechanical properties (Hamad et al. 2018). Currently, synthesis to obtain PLA occurs through two polymerization techniques, the direct condensation of lactic acid monomer, or the opening of the cyclic lactide dimer ring (Nofar et al. 2019), in which the last technique is commonly used industrially for generating PLA polymers with lower production costs and high molecular weight (Hamad et al. 2018; Nofar et al. 2019).

Regarding its properties, PLA has characteristics similar to conventional polymers from petroleum, such as polyethylene terephthalate (PET), polyethylene (PE), polystyrene (PS), polypropylene (PP), and polycarbonate (PC) (Hamad et al. 2018; Koh et al. 2018). PLA when applied as food packaging offers good malleability, resistance to UV light, higher oxygen limit index, lower water absorption rates, and lower processing temperature, when compared to conventional thermoplastics, such as PET (Srivastava et al. 2018; Asgher et al. 2020).

Furthermore, several studies show that the incorporation of additives (e.g., essential oils, plant extracts, and synthetic active compounds) and nanomaterials (e.g., cellulose nanofibers, nanoclay, and metallic nanoparticles) can act improving the physical and mechanical properties of packaging PLA basis. In the incorporation of rosemary, myrtle, and thyme oils in the PLA matrix, Yahyaoui et al. (2016) observed that the films obtained did not show changes in the transparency index, providing materials with less moisture transfer and better mechanical properties, when compared to PLA films without the addition of the oil.

In the study of Mohsen and Ali (2018), the addition of nanoclay provided a reduction of up to 32.38% in the elongation of PLA films; however, the tensile strength and Young's modulus increased 30.06 MPa and 6.4 GPa, respectively. On the other hand, the authors point out that the incorporation of nanoclay in the PLA matrix reduced the oxygen permeability coefficient and the water vapor transmission rate, demonstrating that this nanomaterial can offer better barrier properties when incorporated in PLA films and, consequently, greater protection against moisture and gases when applied on food, extending the shelf life of packaged products.

Bearing in mind that PLA is capable of releasing compounds in a controlled manner, in the area of food packaging, this biopolymer is commonly incorporated with antioxidant and antimicrobial compounds, which promote an increase in the shelf life of food products (Zhang et al. 2020a). Table 4.2 shows some of the studies

Table 4.2 Incorporation of active compounds in PLA matrix

Active compound	Effects in foods	Reference
Thymol, kesum and curry oils	Increased shelf life of chicken meat	Mohamad et al. (2020)
Beta-carotene and lycopene	Preservation and reduction of sunflower oil peroxides	Stoll et al. (2019)
Nanochitosan	Increased shelf life of chilled white shrimp	Fathima et al. (2018)
Green tea extract	Reduced lipid oxidation of smoked salmon	Martins et al. (2018)
α-tocopherol	Oxidative stability of soybean oil	Manzanarez-López et al. (2011)
Natamycin	Mold inhibition on the cheese surface	Lantano et al. (2014)
Fennel oil	Extended shelf life of chilled oysters	Miao et al. (2019)

using PLA incorporated with active compounds that promote a longer shelf life of some food products.

Despite the many applications and advantages of using PLA in the area of food packaging, the reduction in production costs is one of the problems encountered by the polymeric industries, since its value is quite high when compared to oil-derived polymers (Koh et al. 2018). In addition, PLA has a low resistance to breakage compared to commercial polymers, making it more brittle (Zhong et al. 2020). For this reason, the alternatives studied to supply the mechanical and barrier deficiencies found in the PLA are the mixture with other biopolymers, resulting in low-cost biopolymeric blends with better mechanical and barrier properties (Koh et al. 2018; Zhong et al. 2020).

4.4.2 Polyhydroxyalkanoates and Polyhydroxybutyrate

Polyhydroxyalkanoates (PHAs) are biopolymers synthesized through microbial fermentation, being thermostable, having a melting temperature around 180 °C (Srivastava et al. 2018). On an industrial scale, *Cupriavidus necator* is the culture commonly used to obtain PHA in which, in restricted conditions of nutrients and in high concentrations of carbon source, its cells increase in weight and size, accumulating intracellular PHA (Jõgi and Bhat 2020).

PHA has great applicability in packaging development due to its good chemical properties, biocompatibility, resistance to UV light, and ability to be recyclable, being similar to petrochemical thermoplastics (Muneer et al. 2020; Zhong et al. 2020). Through the microbial synthesis of PHA, it is possible to obtain several classes of biopolymers, which are classified according to the size of its carbon chain. Among these PHA classes, the most well-known polymers are PHB and PHBV, which have a high crystallinity index (55–80%) and short chain, representing the most basic forms of commercial PHA available (Muneer et al. 2020).

Regarding its applicability, packaging produced from PHB and PHBV has a high barrier to aromatic compounds and water vapor, preserving and maintaining the quality of packaged foods for a longer time (Muneer et al. 2020; Zhong et al. 2020). In addition, PHBV can be applied in the development of blow-molded beverage packaging, resisting processing temperatures above 200 °C, making it an interesting biopolymer for the development of food packaging (Muneer et al. 2020). PHB films incorporated with eugenol oil were produced, and showed greater crystallinity, and antioxidant and antimicrobial activity, being able to be applied as food packaging (Rech et al. 2020). On the other hand, the incorporation of graphene nanocomposites in the PHB matrix promoted a reduction in the permeability to water vapor and oxygen, and an increase in the melting point, thermal stability, and tensile strength of the developed films (Manikandan et al. 2020). Therefore, the PHA matrix can be easily incorporated with additives that promote better physical, chemical, and mechanical characteristics of the packaging.

However, these polymers have low physical and mechanical resistance, making their industrial and commercial application difficult, when compared to other biodegradable polymers or petroleum derivatives (Meereboer et al. 2020). Therefore, PHB and PHBV when associated with other polymers demonstrate better strength tensile, less fragility, and greater flexibility, being suitable for the development of materials for the medical and food areas. In addition, its high production cost limits its application, having as an alternative the use of food waste as a carbon source during the fermentation process, reducing the costs of the synthesis of PHA polymers (Srivastava et al. 2018).

4.5 Techniques for Improving the Performance of Biodegradable Films

The main restriction in the application of natural polymers in the development of food packaging is due to the poor mechanical and barriers properties in relation to conventional petroleum-based packaging, and therefore, several techniques are developed and used to improve the performance of biodegradable packaging. One of the most used techniques involves mixing two or more natural polymers in the same film-forming solution, developing biopolymeric blends (Asgher et al. 2020). As previously mentioned, biodegradable films are commonly impregnated with nanocomposites (e.g., nanocellulose, nanofibers, and nanoclay) or bioactive compounds (e.g., essential oils, antioxidant and antimicrobial extracts) to provide better mechanical and barrier properties. On the other hand, the crosslinking technique, obtained by physical (e.g., UV lights, hot or cold plasma), enzymatic (e.g., transglutaminase), and chemical agents (e.g., calcium chloride, citric acid, and lactic acid), modifies the structures of natural polymers, improving the physical, mechanical, and barrier properties of biodegradable packaging, expanding the possibility of replacing conventional packaging (Rezaee et al. 2020).

4.5.1 Blends of Natural Polymers

The development of eco-friendly materials that present optimized performance and properties has been obtained over the years, such as the synthesis of blends made from different natural sources. The practice of developing blends for food packaging is a simple alternative for obtaining materials with improved characteristics and properties suitable for application as food packaging (Nogueira and Martins 2019). In general, the formation of blends consists of the mixture of two or more compatible polymers in the same filmogenic solution, obtaining dry films through the technique of casting, thermocompression, or extrusion (Zhong et al. 2020).

Blends from natural polymers are materials developed in order to reduce the impacts caused by the overuse of plastics from petroleum. In addition to the sustainable appeal, the mixture of biopolymers generates materials with improved physical, mechanical, and barrier characteristics due to the intermolecular interactions of polymeric networks, as reported in several studies (Romani et al. 2018; Nofar et al. 2019; Nogueira and Martins 2019; Filipini et al. 2020). Blends can present lower degrees of crystallinity in relation to conventional films, promoting important characteristics for food packaging, such as greater density, transparency, tensile strength, barrier to water vapor, and less flammability (Imre and Pukánszky 2013).

Another relevant point in relation to blends is the modification of the thermal degradation index, the mixture of biopolymers, promote greater stability at low temperatures of the films, enabling their application on chilled or frozen foods (Filipini et al. 2020; Wang et al. 2020). The changes in the thermal properties of blends and greater resistance to changes at high temperatures expand its industrial application, and it can be produced by blowing, extrusion, blow molding, or injection (Zhong et al. 2020). Some examples using blending technology to improve the treatment of film properties can be seen in Table 4.3.

A mixing material that gained attention was curdlan gum for having unique physicochemical properties such as insolubility in water and alcohol (Mohsin et al.

Table 4.3 Effects of biopolymer blends compared to single polymer film

Polymeric matrix	Effects	References
Cassava starch/Chitosan Corn starch/Chitosan	The blend resulted in higher tensile strength	Luchese et al. (2017a)
Gelatin/chitosan	The blend resulted in higher elongation property	Bonilla et al. (2018)
Starch/gelatin	The incorporation of gelatin increased the mechanical properties of the films	Kumar et al. (2019)
Xanthan-Curdlan	Synergistically increased tensile strength	Mohsin et al. (2020)
Whey protein isolate/Chitosan	The blend resulted in the improvement of the mechanical properties	Tavares et al. (2021)
Isolated soy protein/Poly (lactic acid) (PLA)	The incorporation of PLA improved functional properties	González and Alvarez Igarzabal (2013)

2019). According to Wu et al. (2018b), its dispersion in aqueous solutions should help in the formation of gels with better qualitative and mechanical characteristics. In the study of Mohsin et al. (2020) were evaluated the properties of films obtained by combining xanthan and curdlan gums in different proportions. It was observed that individually both polymers have low tensile strength; however, when mixed this property increased. It was also observed that elongation, thickness, and solubility are inversely proportional, with higher values of xanthan gum and lower for curdlan, so the combination can be performed to obtain films with specific properties by varying the concentration of each polymer.

The gelatin/chitosan blend increased the elongation property, compared to the use of each matrix separately; however, for traction and water vapor permeability, the best results were chitosan> chitosan/gelatin> gelatin (Bonilla et al. 2018). When chitosan was combined with corn starch, higher values of tensile strength and elongation were obtained, and higher values of tensile strength were also observed when chitosan was combined with cassava starch compared to the polymer separately (Luchese et al. 2017a).

4.5.2 Crosslinking

The crosslinking process is mainly aimed to modify certain polymer properties, such as chemical and thermal stability, rigidity, permeability, chelation efficiency, protein, and cellular immobilization capacity (Neto et al. 2005; Nair et al. 2020). Nair et al. (2020), state that the number of methods and crosslinking agents found in the literature is many, but the choice of parameters is closely linked to the purpose of the application, given that each agent, method, and type of polymer influence the results obtained from the crosslinking differently.

However, the modifications of the polymers by crosslinking process can be classified by physical or chemical methods (Fig. 4.6).

4.5.2.1 Chemical Crosslinking

The chemical crosslinking method occurs due to the numerous hydroxyl groups (−OH) present in the polymers, and they are susceptible to chemical modifications, such as sulfonation, carboxymethylation, phosphorylation, or hydroxyethylation (Ren et al. 2017a; Dimassi et al. 2018; Musso et al. 2019). From specific agents, all chemical groups along the polymer's backbone can be crosslinked to form "chemical" hydrogels, or "physical" hydrogels from interactions with each other due to ionic and hydrophobic interactions, and molecular entanglements (Pellá et al. 2018). A representation of a crosslinking method is shown in Fig. 4.7.

Several chemical agents are used for the purpose of crosslinking polymers (Xu et al. 2015). The study made by Nair et al. (2020) addresses the main crosslinking agents applied to collagen, as well as their advantages and disadvantages. Among the chemical agents mentioned by the authors are GTA (glutaraldehyde), EDC-NHS ((1-ethyl-3-(3-dimethylaminopropyl) carbodiimide)-

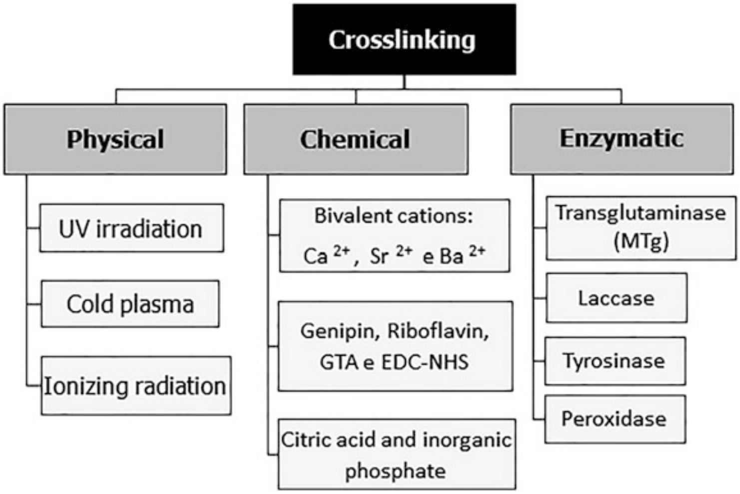

Fig. 4.6 Classification of crosslinking modification methods

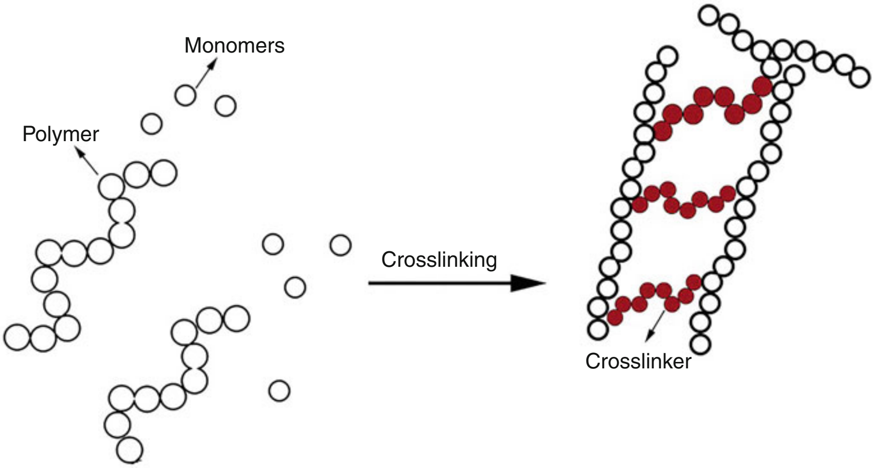

Fig. 4.7 Representation of crosslinking method

NHS (N-hydroxysuccinimide)), genipin, transglutaminase 2, and physical agent, ultraviolet radiation (UV), and DHT (dehydrothermal treatment).

As mentioned throughout this chapter, some natural polymers have poor mechanical and barrier properties, so the crosslinking process is applied to modify and improve these properties. For example, alginate is a hydrophilic polymeric matrix; therefore, its films present low barrier properties. According to Benavides et al. (2012) and Rhim and Wang (2014), making a crosslink with polyvalent cations is an alternative to improve its water barrier properties, mechanical resistance, cohesiveness, and rigidity.

The addition of certain cations to the alginate solution leads to the formation of a gel through ion exchange (Lu et al. 2006). Among the most used cations, calcium (Ca^{2+}), strontium (Sr^{2+}), and barium (Ba^{2+}) (Lee and Rogers 2012) stand out. Calcium ions are more used to crosslink alginate, especially calcium chloride (SenturkParreidt et al. 2018). Ca^{2+} sources influence the rate of gel formation and its concentration. Thus, it is possible to obtain films with less permeability to water vapor and greater resistance (Cazón et al. 2017).

Another agent used for crosslink films is citric acid, which has the advantage of being nontoxic, low cost, and capable of improving the functional properties of the film (Amanatidou et al. 2000). Kumar et al. (2019) showed that films made with citric acid crosslinked starch showed good tensile and barrier properties and also improved solubility in water; however, the films showed low elasticity. Some crosslinking agents are not used for food packaging, as copper, zinc, lead, and cobalt (SenturkParreidt et al. 2018).

According to González et al. (2011), the polymer chain of chitosan can be crosslinked by different agents, such as metallic ions (Ag^{+}, $Hg^{2\ +}$, and Cu^{2+}), and the authors also state that studies demonstrate greater resistance to dissolution in acid medium, less hydrophilicity, and reduced chemical reactivity of the material prepared from crosslinked chitosan. The characteristics of chitosan and the reaction conditions will affect the crosslinking process (Berger et al. 2004).

According to Xu et al. (2015), chemical modifications in the structure of polysaccharides and proteins (starch, cellulose, gelatin, gums, etc.) can be carried out by various crosslinking agents, and in general, the mechanism is used for the same purpose, to improve the properties of polymers to enhance their use in biodegradable packaging.

4.5.2.2 Enzymatic Crosslinking

The application of enzymatic crosslinking occurs mainly in protein matrix (e.g., collagen, gelatin, and casein) due to the damage of structures caused during the dissociation and/or extraction process of the biopolymer (Duan et al. 2020). The use of enzymes to promote the crosslinking process has been showing positive effects in the formation of films, generating materials resistant to water and with better mechanical, barrier, thermal, and morphological properties (Liu et al. 2017).

According to Wu et al. (2018a, b), the application of enzymatic crosslinking has a nontoxic characteristic, high efficiency, and viability, since the enzymes are GRAS-certified and are usually used in the food industry (e.g., transglutaminase, laccase, tyrosinase, and peroxidase). In this context, enzymatic crosslinking comprises the approximation and formation of inter- or intramolecular covalent bonds of protein molecules, without the formation of toxic and harmful compounds to human health, providing safe control to the process when compared to the chemical crosslinking (Isaschar-Ovdat and Fishman 2018).

Due to its wide availability, ease, and low cost to obtain in relation to the others, the commercially available enzyme transglutaminase (MTg) is widely used in the food industries to promote changes in the texture of protein products, inducing gelation cold and/or joining protein molecules (Romeih and Walker 2017; Isaschar-Ovdat and Fishman 2018). MTg shows optimum activity at pH between 5 and 7 and in the temperature range of 40–50 °C, being inactivated by exposure to temperatures above 70 °C (Romeih and Walker 2017).

Gelatin films crosslinked with transglutaminase showed a solubility reduction of up to 80% (Liu et al. 2017). Films composed of coconut protein and guar gum showed better mechanical, barrier, and thermal properties when treated with MTg. The crosslinking promoted by the enzyme increased the interaction between the two biopolymers. On the other hand, when inserting the enzyme oxidase tyrosinase in casein films, Juvonen et al. (2011) obtained materials with lower values of solubility and smaller contact angle, enabling the application of this biomaterial as packaging for foods with higher moisture content.

4.5.2.3 Plasma Technology

Plasma is considered the fourth state of matter in the world. With the increase in the energy level, the state of matter is changed from solid to liquid, then to gas, and finally to plasma (Pankaj et al. 2014c). The term "plasma" refers to an almost neutral ionized gas, which can be explained by the existence of an equal number of positive and negative charges carried by different species, composed mainly of ions, electrons, photons, and atoms in their fundamental states or excited (Pankaj et al. 2014b; Sharma and Singh 2020).

Plasma is generally divided into two categories, thermal and nonthermal (cold plasma) that depend on the condition in which they are generated (Pankaj and Thomas 2016). The thermal process occurs when operated at high pressure and temperature and requires great power to produce it, and this occurs when electrons and other types of gases are in thermodynamic equilibrium. Nonthermal process is when the operation occurs at low pressure, requiring less operating energy (Hati et al. 2018). Plasma can be generated by radio frequency (RF), direct current (CD), or microwave (MW) applied to the precursor gas used in the application (Sharma and Singh 2020).

There are several options to choose the carrier gas. Gases such as air, nitrogen, oxygen, helium, or argon can be used individually or combined at plasma technology, and the basic advantage of using air as a transport gas is its availability and low cost (Niemira 2012). Misra et al. (2014) reported that plasma chemistry depends on several factors, such as the composition of the feed gas, humidity, energy, applied voltage, and surrounding stage.

The interaction of the compounds generated by the plasma gas discharge with the different groups of the polymer molecules will form polar hydrophilic groups improving the adhesion and wettability properties, allowing the retention of active molecules and other compounds on the polymer surface, as representing in Fig. 4.8. These changes in polymer surfaces through the use of cold plasma have the advantage of not using hazardous solvents, in addition the treatment is uniform and does not cause thermal damage when in contact with the materials, which allows it to be used in temperature-sensitive biomaterials (Morent et al. 2011).

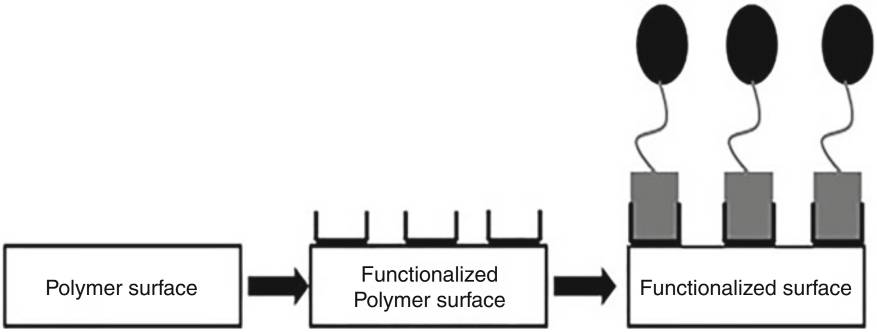

Fig. 4.8 Representation of the functionalization of surfaces by plasma technology (Source: Adapted from Goddard and Hotchkiss (2007))

The use of cold plasma to improve the properties of biopolymers has attracted attention in research such as the use of chitosan (Demina et al. 2012; Chang and Chian 2013), polylactic acid (Pankaj et al. 2014b; Benetto et al. 2015), starch (Albuquerque et al. 2014; Benetto et al. 2015; Pankaj et al. 2015a), zeina (Pankaj et al. 2014c; Gezer et al. 2015), gelatin (Demina et al. 2012; Pankaj et al. 2015b), fish protein (Romani et al. 2019), and defatted soy flour (Oh et al. 2016) are some examples where treatment with cold plasma was performed.

Cold plasma technology has applications in several fields, such as textile processes, sterilization, biological sciences, packaging, and drug distribution systems (Samanta et al. 2010; Luna et al. 2011; Hagiwara et al. 2013). It presents several promising applications for the food industries such as food decontamination, toxin degradation, food process causing modification of the functionality of food components, equipment sterilization, air filtration, wastewater remediation, improved germination performance of seeds, improvement in the physicochemical properties of grains, degradation of agrochemical residues, and packaging surface treatments (Pankaj and Thomas 2016).

According to Ren et al. (2017b), cold plasma treatment is an environmentally friendly process, since it is free of chemicals and does not produce waste. It is an example of a dry process suitable for materials sensitive to heat that do not pollute the environment (Chu et al. 2002; Pankaj et al. 2014a; Mahmoud 2016).

There are several rapidly expanding technologies that have been used to generate cold plasma. Since they can operate at atmospheric pressure or in a vacuum, ionized gas can be as simple as air or nitrogen, or it can be a more complex mixture using noble gases, as helium, argon, or neon (Niemira 2012).

Among the plasma systems most used to modify the surfaces of the films, the low-pressure luminescent discharge (DC) stands out, which is formed when a sufficiently high potential difference is applied between two electrodes placed in a gas, the latter will divide into positive ions and electrons, giving rise to a discharge of it (Pankaj et al. 2014a). The atmospheric pressure plasma jet method (APPJ) is

Table 4.4 Source of plasma and polymers used

Plasma source	Polymers	Reference
Low pressure luminescent discharge (DC)	Fish myofibrillar proteins	Romani et al. (2019)
	Whey protein and gluten	Moosavi et al. (2020)
	Fish proteins	Romani et al. (2019)
Dielectric barrier discharges (DBD)	Polylactic acid (PLA)	Pankaj et al. (2014b)
	Bovine gelatin	Pankaj et al. (2015b)
	PLA/microfibrillated cellulose (MFC)	Meriçer et al. (2016)
	Zein/Chitosan	Chen et al. (2019)
	Casein	Wu et al. (2020)
	PLA coated zein	Chen et al. (2020)
	Sodium caseinate	Jahromi et al. (2020)
	Isolated pea protein	MahdavianMehr and Koocheki (2020)
Atmospheric pressure cold plasma (ACP)	Isolated whey protein	Segat et al. (2015)
	Defatted soybean meal (DSM)	Oh et al. (2016)
	Zein	Dong et al. (2018)

generated when rare gases, such as helium or argon, are used to generate cold plasma even under atmospheric pressure (Ojha et al. 2021).

In dielectric barrier discharge (DBD), plasma is generated between two metal electrodes, at least one of which is covered by a dielectric layer that has the role of limiting the discharge current by preventing the transition of the arc and randomly distributing its coils on the electrode surface for homogeneous treatment (Tendero et al. 2006; Pankaj et al. 2014c). Another method used for cold plasma generation is cold plasma at atmospheric pressure (ACP), which can be obtained by exposing a gas or mixture of gases to an electric field, and it accelerates the charged particles, resulting in collisions with heavy species (as ions and neutrals) (Attri et al. 2013; Sadhu et al. 2017).

Studies show that treatment with cold plasma can induce various physical and chemical changes in the plasma surfaces. Some sources of plasma are more used in the modification of film surfaces, and Table 4.4 presents some polymers and the source of plasma used to obtain improvements in the characteristics of the films.

Romani et al. (2019) functionalized fish protein films, using cold plasma (luminescent discharge) and coated with carnauba wax. The application of luminescent discharge plasma followed by carnauba wax coating resulted in an increase of 175% in the tensile strength and 65% less water vapor permeability in fish protein films compared to control films.

Moosavi et al. (2020) studied the influence of different cold plasma treatments to modify the properties of whey and gluten protein film. The authors report that the films treated with low-pressure vacuum luminescent discharge plasma showed an increase in the tensile strength 10 min of processing, from 6.9 to 10.7 MPa and from 1.8 to 2.5 MPa for whey and gluten protein films, respectively.

The exposed above indicate that the plasma source, working gas, type of protein, sample volume, and treatment medium play an important role in plasma application, inducing denaturation/modification of proteins. The targeted functionalization can offer another innovative approach for specific modification of the functional properties of films.

4.5.2.4 UV Irradiation

The application of irradiation by UV light can promote the crosslinking of biopolymers, causing the modification and improvement of the characteristics of biodegradable materials. UV irradiation is a physical crosslinking technique that has several advantages over other types of crosslinking, highlighting its simplicity, environmental friendly, and low costs, eliminating the use of chemical agents in the process (Rezaee et al. 2020). In addition, UV irradiation has no negative effects on human health, being applied as a technique to reduce and inactivate a wide range of microorganisms (Bigi et al. 2020). UV irradiation is classified into UV-A (315–400 nm), UV-B (280–315 nm), and UV-C (200–280 nm) according to the wavelength region, and this technique can cause modifications in the polymer chains from exposure of the film-forming solution or pre-formed film (Fathi et al. 2018) as shown in Fig. 4.9.

During the exposure of films to UV irradiation, the molecules become excited, causing chain splitting, crosslinking, and oxidation (Sionkowska et al. 2010). In addition, the increase in chemical reactions from photo-oxidative degradation modifies the surfaces of polymers, generating reactive sites in which they can immobilize various active compounds (e.g., metallic nanoparticles, bioactive compounds, and antimicrobial agents), which can improve the characteristics of the packaging (Alonso et al. 2009). However, the time of exposure to UV irradiation must be accurately determined for each type of material, since the permanence to UV light for long periods can damage and impoverish the characteristics of biopolymers due to photodegradation that, in the first instance, destroys interactions of

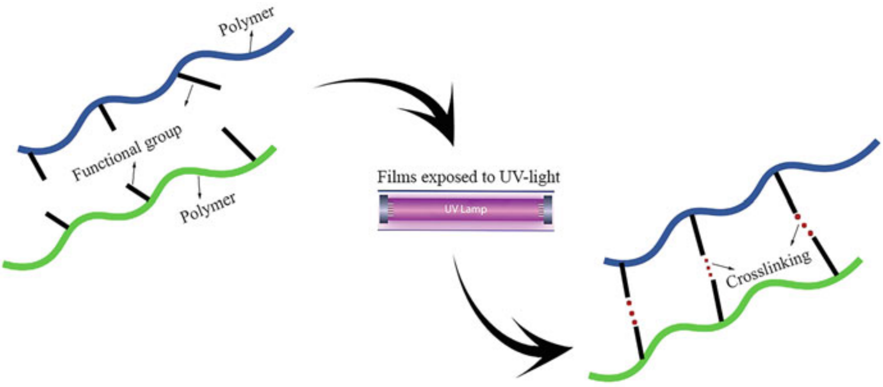

Fig. 4.9 Representation of the crosslinking system in polymers using UV-light

Table 4.5 Effects of UV irradiation on biodegradable films

Biopolymer	Effects on materials	Reference
Isolated sesame protein	Increased crystallinity index Compact structure formation Reduced moisture content, solubility and water vapor permeation Increased hydrophobic density of films Greater tensile strength and Young modulus	Fathi et al. (2018)
Whey protein isolate	Modification of the tertiary structures of proteins Reduction of solubility Increased surface hydrophobicity	Kristo et al. (2012)
Whey protein concentrate	Structural modifications of proteins Different color of the films Increased tensile strength of films	Díaz et al. (2016)
Blend of collagen/ chitosan	Reduction in tensile strength and elongation of films Increased of Young modulus	Sionkowska et al. (2006)
Blend of chitosan/ keratin	Reduction of traction, elongation and Young modulus Increased surface polarity of films	Sionkowska et al. (2010)

noncovalent polymer chains and then breaks the covalent bonds of the matrix, resulting in reductions in physical, mechanical, and barrier properties (Sionkowska et al. 2015).

In relation to protein-based films, the nondestructive and moderate effects of UV irradiation under suitable conditions cause desirable changes in the physical and mechanical properties of protein materials (Rezaee et al. 2020). Several studies demonstrate the efficiency of using UV irradiation in collagen and gelatin films. This efficiency occurs because proteins are one of the main targets of UV light, inducing several physical–chemical processes to the biopolymeric network, promoting expansion and chemical stability (Stylianou et al. 2014).

Table 4.5 shows some effects of the UV light on the surface of the biopolymer-based materials.

4.6 Conclusion

One of the main functionalities of the packaging is the preservation and extension of the shelf life of food products, reducing waste and promoting greater safety in the consumption of food products. Biodegradable packaging becomes an alternative to conventional packaging, since it can reduce the impacts caused by the excessive use of synthetic materials. However, biodegradable materials have poor mechanical and barrier properties in relation to synthetic packaging, hindering their diffusion in the industrial area. Despite this, studies show that the application of some techniques can expand the applicability of biodegradable materials. However, it is increasingly necessary to develop more studies in relation to the effects of applying these techniques to improve the performance of bio-based films, in order to improve their properties, making them more competitive in the packaging market.

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Smart Freshness Indicator for Animal-Based Product Packaging: Current Status

5

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Abstract

Freshness is one of the most significant attributes for monitoring the quality of animal-based products. During product supply chain, freshness of animal-based products decreases, along with the product quality and safety. In order to meet the consumer preferences for the fresh and safe products, smart freshness indicator has been developed. Smart freshness indicator is a device that can indicate degree of freshness and provide directly information about the quality of product based on microbial growth or metabolites in packaged products through direct color visual change. The application of smart freshness indicator has become increasingly interesting because it can provide convenience, enhance safety, and provide information to consumer. According to its benefits, much research is published every year focusing on evaluation of animal-based product freshness using freshness indicator. Therefore, smart freshness indicator could be helpful in assuring the quality and safety of packaged products.

Keywords

Animal-based products · Freshness indicator · Quality · Smart packaging

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5.1 Introduction

Animal-based products (meat, poultry, fish, and seafood) are classified as highly perishable foods. They are rich in nitrogenous substances, carbohydrates, and lipids with a pH of $\geq$6 and water activity (a_w) greater than 0.97 (Erkmen and Bozoglu 2016). These factors are favorable for microorganism growth (bacteria, yeasts, and molds) and biochemical reactions. Microorganisms can cause unacceptable changes with the formation of various metabolites in animal-based products. Microbial-generated metabolites (e.g., biogenic amines (e.g., cadaverine, histamine, putrescine, tyramine), carbon dioxide, ethanol, organic acids, sulfuric compounds (hydrogen sulfide), and volatile nitrogen compounds (ammonia, dimethylamine, and trimethylamine described as total volatile basic nitrogen; TVB-N)) are mostly found in animal-based products (Rukchon et al. 2014; Smolander 2003). As is known, the spoilage process always generates during storage, transport, and retailing, and in consumers' homes, which is correlated with the organoleptic changes. However, it is hard to believe decision by evaluating the organoleptic analysis of products and traditional quality analysis method has complicated and time-consuming procedures. Thus, the development of new technologies with accurate, convenient, cost-effective, rapid, and nondestructive method to evaluate quality and safety of animal-based products is a great needed.

Intelligent or smart packaging is defined as packaging that contains an internal or external indicator to provide information about aspects of the history of the package and/or the product quality directly (Robertson 2012). Smart packaging has been currently focused because it has a function for freshness indication. A smart freshness indicator can be made from biopolymer material (solid support) incorporated with dye indicator (chemical and natural dye indicators). The consumers are currently concerned about the use of chemical dye indicators in food packaging system because of their possible toxicity and potential risk to human health. So, its use is restricted as dye indicator. Many natural dye indicators have been effectively incorporated into biopolymer films. Some include anthocyanin (Liu et al. 2019; Rawdkuen et al. 2020; Zeng et al. 2019), betalains (Kanatt 2020; Qin et al. 2020; Yao et al. 2020), and curcumin (Chen et al. 2020; Liu et al. 2018). Smart freshness indicators are able to indicate the product quality directly by changes in color in the real time, resulting from the reaction between the presence of generated metabolites and the smart freshness indicators during loss of freshness. Thus, smart freshness indicators are a promising tool to inform product quality and safety to consumers and suppliers via real-time and rapid qualitative analysis (through visible color changes by naked eye) at any given time. Recently, many research studies have successfully used natural dye indicators and then applied in a real food system. For example, smart freshness indicators can be used as an effective tool for the real-time monitoring of meat, poultry, fish, and seafood products during storage (Chen et al. 2019; Dudnyk et al. 2018; Mohammadalinejhad et al. 2020; Moradi et al. 2019).

In this chapter, the compounds indicating the quality of packaged animal-based products are presented. Subsequently, the concept of smart freshness indicators and the potential sources of dye indicators are reviewed. The current researches on the applications of smart packaging with a function of freshness indication on various animal-based products are also discussed.

5.2 Compounds Indicating the Quality of Packaged Animal-Based Products

Freshness is a critical variable that affects the organoleptic properties and food product acceptability (Cardello and Schutz 2003). The freshness of animal-based products is reduced in time as a result of microbial growth or chemical changes. Loss of freshness indicates that animal-based products have started to spoil. Difference in formation of metabolites in animal-based products is affected by the nature of product, associated spoilage flora, packaging system, and storage conditions (Kerry 2012; Smolander 2003). During storage, transport, and retailing, various metabolites are generated in animal-based products such as biogenic amines (e.g., cadaverine, histamine, putrescine, tyramine), carbon dioxide (CO_2), ethanol, organic acids, sulfuric compounds [hydrogen sulfide (H_2S)], and volatile nitrogen compounds [ammonia (NH_3), dimethylamine (DMA; $(CH_3)_2NH$), and trimethylamine (TMA; $(CH_3)_3N$) described as total volatile basic nitrogen (TVB-N)] due to microbial growth and metabolism (Rukchon et al. 2014; Smolander 2003). Animal-based products are composed of free amino acids; proteins in animal-based products are broken down into amino acids by hydrolysis. As a result, they can be partially or totally degraded into simple compounds such as CO_2, H_2O, NH_3, and H_2S (Rukchon et al. 2014). Currently, most research studies have developed metabolite indicators associated with animal-based products such as CO_2, H_2S, and TVB-N produced during storage by microbial degradation of protein-rich foods. Some of the metabolites or compounds indicating the quality of packaged animal-based products representing potential target marker metabolites for the smart freshness indicators are discussed in detail.

5.2.1 Biogenic Amines

Biogenic amines are known as a toxic substance. They have been employed as indicators of hygienic quality, freshness quality index, and control the processing of muscle-based products (Ruiz-Capillas and Herrero 2019; Smolander 2003). The most important biogenic amines substance found in food are cadaverine, histamine, putrescine, and tyramine. Fish and fishery products are abundant in histamine. The hazard potential of biogenic amines should be considered due to their physiological and toxicological effects, and risk to human health. In the USA, Food and Drug Administration (FDA) has set histamine limits in fish and fishery products in general at 50 mg/kg (Ruiz-Capillas and Herrero 2019). Kung et al. (2017) studied the effect of polyethylene packaging (PEP) (in air) and vacuum packaging (VP) on histamine changes in milkfish sticks during storage. They found that milkfish sticks packaged with VP had lower levels of aerobic plate count (APC), TVB-N, and histamine than milkfish sticks packaged with PEP.

5.2.2 Carbon Dioxide

Carbon dioxide (CO_2) is mainly generated during microbial growth (Smolander 2003). It can be used to indicate the quality deterioration. Increased CO_2 concentrations are frequently accompanied by increasing the storage time (Lee et al. 2019). However, the indication of microbial growth by CO_2 may be difficult in some packaging technology system like modified atmosphere packaging (MAP) because MAP already containing high concentration of CO_2 (typically 20–80%) (Kerry 2012). Lee et al. (2019) developed a freshness indicator based on poly(ether-block-amide) incorporated with bromocresol green for the real-time monitoring of quality changes in chicken breasts during storage at 4 and 10 °C for 10 days. They found that changes in color (from yellow to green) of freshness indicator were correlated with CO_2, TVB-N, and bacterial growth in the chicken breast.

5.2.3 Organic Acids

Organic acids, such as lactic acid and acetic acid, are the main compounds having a role in glucose fermentation by lactic acid bacteria (Smolander 2003). Zhao et al. (2019) found that the concentration of lactic acid, acetic acid, and succinic acid in tilapia fillet increased with increasing storage time. They also suggested that organic acids were related to fish spoilage.

5.2.4 Ethanol

Ethanol is another major end product of fermentative metabolism of lactic acid bacteria. Zhao et al. (2019) found an increase in the amount of ethanol concentration in tilapia fillet during refrigeration storage. The formation of ethanol can contribute to unfavorable fishy odor.

5.2.5 Sulfuric Compounds

Hydrogen sulfide (H_2S) is produced from cysteine. It forms a green pigment, sulfmyoglobin, when it is bound to myoglobin (Smolander 2003). It has a remarkable effect on the sensory quality of animal-based products due to their off-flavor and low odor threshold. H_2S and other sulfuric compounds have been found to be produced during the spoilage of meat, poultry, and seafood by a number of bacterial species. *Shewanella* are H_2S-producing and responsible for seafood spoilage markers when stored at low temperature (Zhu et al. 2015).

5.2.6 Volatile Nitrogen Compounds

Volatile nitrogen compounds are ammonia, dimethylamine, and trimethylamine, which are responsible for quality and spoilage of fish (Kung et al. 2017). These compounds (ammonia, dimethylamine, and trimethylamine) are described as TVB-N. TVB-N is formed during storage due to endogenous enzymes and microbial activities, resulting in the formation of compounds. TVB-N increases as the fish freshness decreases. Currently, the use of anthocyanin as natural dye indicator for the determination of volatile nitrogen compounds has been suggested in many studies (Chen et al. 2020; Dudnyk et al. 2018; Kang et al. 2020).

5.3 Smart Freshness Indicators

Indicators are tools or devices that provide information about the absence or presence of substance or the degree of reaction between two or more substances by changing characteristic like color (Hogan and Kerry 2008). Most often, they provide qualitative information through directly visible color change (different product's status exhibits differences in color intensities). Indicators can be divided into three categories of time–temperature indicators, gas indicators, and freshness indicators. According to Robertson (2012), all of the indicators are group of product quality and value-improving systems, which are frequently used for intelligent food packaging applications.

Smart freshness indicators are produced in the form of labels or tags, and then attached inside the packaging materials. They have been developed with the aim of the real-time monitoring of the quality and safety of packaged food products through visible color changes, which can be directly observed by the naked eye. Changes in color of indicators should be noticeable even at the minimal spoilage level of the packaged food products. The concept of smart freshness indicators is based on changes in color of the indicators due to the presence of microbial-generated metabolites during loss of freshness. The smart freshness indicators accurately track the increase in concentration of metabolites in the package headspace. They may share information about the packaged animal-based product quality and safety directly to the consumers and suppliers at any given time. They can also alert the consumers and suppliers about the degree of freshness. Thus, the consumers and suppliers can decide that the packaged product should be distributed or retailed or consumed or discarded (Fig. 5.1). The major advantages of smart freshness indicator are sensitive, can be detected by naked eye, and are easy to be integrated into packaging system. However, the disadvantage of smart freshness indicators is false-negative results. This problem should be resolved before widespread commercial uptake to prevent producers from adopting indicators in the use of real situation. Furthermore, an exact correlation between target metabolites, product type, and organoleptic quality and safety is necessary to avoid false negatives (Smolander 2003). Currently, smart freshness indicators have been proposed, for example, for CO_2 and TVB-N.

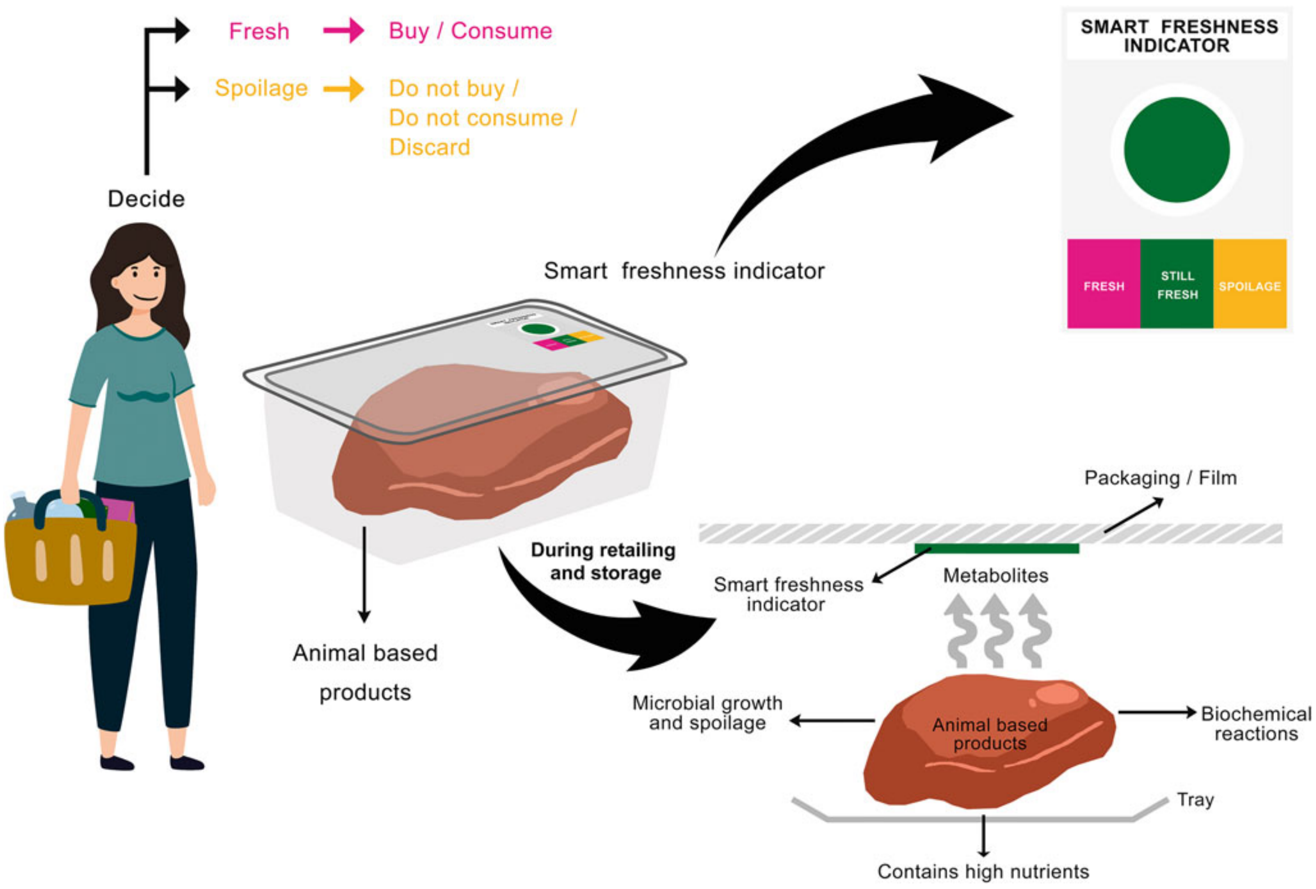

Fig. 5.1 Concept of smart freshness indicator

5.4 Sources of Dye Indicators

There are two major sources of dye indicators: chemical dye indicators and natural dye indicators. Currently, the consumer preferences have shifted the attention of dye indicators from chemical to natural because natural dye indicators are safe, renewable, and have no harmful effects of the human health. Dye indicators are generally added to packaging material to produce intelligent packaging. They can alert the quality and safety of packaged products to consumer during retailing and storage through visible color changes.

5.4.1 Chemical Dye Indicators

Chemical dye indicators are also commonly known as acid–base indicators or pH indicators, belonging to two different families: Sulfonephthalein and Azo (Pastore et al. 2021). Most of these indicators are organic and synthetic origin. They are dye substances, which can change color as a result of exposure to different conditions (e.g., variation of pH and concentration of gases) (Pastore et al. 2021). Most of them are soluble in organic solvent but insoluble in water. They have been widely used in the industry such as food packaging industry (pH sensor device for monitoring food spoilage), cosmetics, detergent industry, and textile industry. However, the current trend of chemical dye indicators is not acceptable due to their toxicity (e.g., acute toxicity, carcinogenicity, mutagenicity, and genotoxicity), which may affect consumer's health (Sabnis 2007). The consumer preferences have shifted the attention of manufacturers from chemical to natural dye indicators. They are also limited in the pH range because they showed very narrow color, which are difficult to observe by the naked eye. For example, bromocresol green has only three color transitions: yellow (pH 3.8), green (pH range 3.8–5.4), and blue (pH 5.4). Thus, the combination of two or more chemical dye indicators is needed for effectively enhancing their pH indication. Example and color changes in chemical dye indicators frequently used in the intelligent packaging are summarized in Table 5.1.

5.4.2 Natural Dye Indicators

Recently, there is becoming increasingly important in smart freshness indicator made up of natural dye indicator and natural biopolymer materials, owing to their nontoxic material, safe, eco-friendly, renewable, and biodegradable that might replace chemical one. Various compounds that found in natural source have interesting potential for use as dye indicators. Currently, many research studies focus on natural dye pH sensing indicators such as anthocyanin, betalains, and curcumin due to their nontoxic, renewable, and safe. All of these compounds could be a good source of dye indicator material. Many studies have demonstrated a promising of natural dye indicators for potential development of smart packaging systems (Table 5.2).

Table 5.1 Examples and color changes in chemical dye indicators

Chemical dye indicators	pH range	Indication (color changes)
Alizarin red	5.5–6.8 10.1–12.1	From yellow to red From red to purple
Bromocresol green	3.8–5.4	From yellow to blue
Bromocresol purple	5.2–6.8	From yellow to purple
Bromophenol blue	3.0–4.6	From yellow to blue-purple
Bromophenol red	5.2–6.8	From yellow to red
Bromothymol blue	6.0–7.6	From yellow to blue
m-Cresol purple	1.2–2.8 7.4–9.0	From red to yellow From yellow to purple
o-Cresol red	0.2–1.8 7.0–8.8	From red to yellow From yellow to reddish purple
Methyl orange	3.0–4.4	From red to yellow
Methyl red	4.4–6.2	From red to yellow
Methyl yellow	2.9–4.0	From red to yellow
Phenolphthalein	8.0–10.0	From colorless to pink
Phenol red	6.8–8.4	From yellow to red
Resazurin	3.8–6.5	From orange to purple-violet
Thymol blue	1.2–2.8 8.0–9.6	From red to yellow From yellow to blue

Source: Sabnis (2007)

Anthocyanin is water-soluble phenolic pigments, belonging to the family flavonoids. It is responsible for red, pink, purple, and blue color of plants. It can be extracted from barberry (Alizadeh-Sani et al. 2021), butterfly pea (Rawdkuen et al. 2020), mulberry (Zeng et al. 2019; Zhang et al. 2020), purple sweet potato (Choi et al. 2017; Jiang et al. 2020), red cabbage (Dudnyk et al. 2018; Liu et al. 2021; Vo et al. 2019), and roselle (Zhang et al. 2019). Color changes in anthocyanin are mostly due to modification of chemical structure of phenolic substances. The structure of anthocyanin changes at different pH values (Miguel 2011). Anthocyanin can change its color with wide ranges when the pH changes. Butterfly pea anthocyanin extract solution had red color, pink color, violet or purple color, blue color, and turned to green color when the pH of butterfly pea anthocyanin extract solution was 2, 3, 4–6, 7, and 7–12, respectively (Rawdkuen et al. 2020). Red cabbage, sweet potatoes, butterfly pea, mangosteen, and mapring seed have been reported to be suitable natural sources of anthocyanin extraction and can be added into biopolymer films for developing smart indicator (Rawdkuen et al. 2020). Mohammadalinejhad et al. (2020) suggested that the film based on bacterial cellulose with *Echium amoenum* anthocyanin is highly sensitive to detect TVB-N by visually distinguishable color changes (fresh: violet, use soon: gray, spoiled: yellow) of shrimp and the incorporation of *Echium amoenum* anthocyanin can be beneficial for monitoring protein-rich food spoilage.

Betalains are water-soluble pigments, which are composed of a nitrogenous core structure of betalamic acid [4-(2-oxoethylidene)-1,2,3,4-tetrahydropyridine-2,6-

Table 5.2 Examples and color changes in natural dye indicators

Sources	pH range	Indication (color changes)	References
Anthocyanin			
Mulberry	2.0–11.0	From bright red to dark green	Zeng et al. (2019)
Butterfly pea	2.0–12.0	From red to green	Rawdkuen et al. (2020)
Purple sweet potato	2.0–12.0	From red to green and yellow	Jiang et al. (2020)
Jambolan (*Syzygium cumini*) fruit	1.0–13.0	From red to yellow	Merz et al. (2020)
Echium amoenum	2.0–12.0	From red to yellow	Mohammadalinejhad et al. (2020)
Black carrot	2.0–11.0	From red to gray	Moradi et al. (2019)
Lycium ruthenicum Murr.	2.0–10.0	From pink to yellow	Liu et al. (2019)
Betalains			
Red pitaya (*Hylocereus polyrhizus*) peel	3.0–12.0	From red to yellow	Qin et al. (2020)
Amaranthus leaf	1.0–9.0	From pink to yellow	Kanatt (2020)
Cactus pears (*Opuntia ficus-indica*)	3.0–12.0	From purple/red to orange/yellow	Yao et al. (2020)
Curcumin			
Turmeric	3.0–10.0	From yellow to red and then reddish brown	Liu et al. (2018)
Turmeric	5.0–11.0	From yellow to light yellow and then reddish brown	Chen et al. (2020)

dicarboxylic acid] (Rahimi et al. 2019). Betalamic acid can either condense with imino compounds (cyclo-DOPA) to form red/violet betacyanins, or with amines and their derivatives to form yellow/orange betaxanthins (Prieto-Santiago et al. 2020). They are obtained from plants such as amaranth, red pitaya, red beetroot, cactus pears, and prickly pear (Kanatt 2020; Qin et al. 2020; Rahimi et al. 2019; Yao et al. 2020). In alkaline conditions, they have variations in color from red to yellow and their structures are largely stable in the pH range of 3–7 (Qin et al. 2020). Betalains have broader pH stability than anthocyanins (Kanatt 2020). They also possess various biological properties such as antioxidant, antimicrobial, anti-inflammatory, anticancer, and anti-lipidemic (Kanatt 2020; Prieto-Santiago et al. 2020). Betalains have a potential for being used as dye indicator in intelligent packaging. Qin et al. (2020) developed intelligent film from red pitaya (*Hylocereus polyrhizus*) peel extract incorporated in starch/polyvinyl alcohol film. They reported that developed intelligent film could be effectively presented as visual color changes and could be used as intelligent film for monitoring food freshness. Kanatt (2020) suggested that the incorporation of betalains extracted from *Amaranthus* leaf into polyvinyl alcohol/gelatin film could help to alert the consumer to know the food begins to spoil due to visible color changes (from red to yellow).

Curcumin is a natural polyphenol compound found in the rhizome of *Curcuma longa* (turmeric) and in others *Curcuma* spp. (Hewlings and Kalman 2017). It represents the main curcuminoid of turmeric and is responsible for the intense yellow color. It is widely used as a spice, medicinal herb, and colorant. It has several pharmacological activities such as antimicrobial, antioxidant, anti-inflammatory, and anticancer properties (Hewlings and Kalman 2017; Liu et al. 2018). Liu et al. (2018) studied the color changes in curcumin solutions in a wide pH range (3–10) and found that the color of curcumin solutions changed from bright yellow to reddish brown with increasing pH values. However, the color changes in curcumin solutions are difficult to distinguish in pH range from 3 to 7 and may affect to judge freshness of product accurately. Chen et al. (2020) developed freshness indicator based on starch/polyvinyl alcohol containing curcumin, anthocyanin, and mixture of curcumin and anthocyanin. The films containing curcumin had greater color stability than the films incorporated with anthocyanin when stored at 25 °C for 180 days. They also reported that the incorporation of a mixture of curcumin and anthocyanin in a ratio of 2:8 (v/v) into films exhibited good color indication and significant change in color for fish freshness during storage at 4 °C for 10 days.

5.5 Applications of Smart Freshness Indicator

The quality and safety of packaged animal-based products continuously decrease with increasing storage time. Freshness is basic characteristic for judging the quality and safety of packaged animal-based products. The loss of packaged product freshness means packaged product has begun to spoil. Animal-based products are classified as highly perishable foods due to their richness in nutrients, resulting in susceptibility to microbial contamination and biochemical reactions. The metabolites generated by spoilage microorganisms affect quality and safety of packaged products. Recently, the consumers are more concerned about animal-based product quality, safety, and their health. Consumers generally know the freshness of food products through checking “best before” or “expiration date” that label on the package or sensory method. However, it is hard to believe decision by evaluating the overall appearance or texture of animal-based products. In recent years, so-called smart freshness indicator has emerged as an alternative method for monitoring animal-based product freshness. Thus, smart freshness indicator for the real-time evaluation of highly perishable food quality like meat, poultry, fish, and seafood is needed.

5.5.1 Meat Products

Meat products are extremely highly perishable food. They have a very short shelf life, usually 3–4 days at refrigerated storage, owing to microbial contamination and biochemical reactions. They contain adequate amounts of essential nutrients, which support the growth of microorganisms. Various metabolites are produced by microorganism associated with food spoilage, leading to off-flavor, off-odor, discoloration, and nutritional loss. These effects result in pH variation in the packaged meat products. Generally, it is difficult to detect spoilage of packaged meat through the naked eye. Thus, meat product industry requires rapid, inexpensive, simple, and nondestructive tool or device for naked eye and real-time monitoring of the degree of freshness of packaged meat products. Smart freshness indicator is an effective tool for evaluating packaged meat quality and safety. Recently, various natural dye indicators are increasingly interested in developing smart freshness indicator such as purple sweet potato (Choi et al. 2017), barberry (Alizadeh-Sani et al. 2021), roselle (Zhang et al. 2019), and red cabbage (Dudnyk et al. 2018; Liu et al. 2021; Vo et al. 2019). These natural dye indicators can effectively sense packaged meat product spoilage, exhibiting through visual color changes. Thus, the consumer can know information about the packaged meat quality and safety by the naked eye through the visible color changes in smart freshness indicator on the package. Several smart freshness indicators have been developed with the aim of monitoring meat product freshness (Table 5.3).

5.5.2 Poultry Products

Poultry products are classified as highly perishable food. They usually deteriorate rapidly (within 1 week of slaughter) because they are susceptible to physicochemical and biological changes. They are rich in proteins (made up of 18%) and are composed of approximately 75.5% water (Cutter et al. 2012). The presence of water in poultry tissue affords microorganism with another component to support microbial growth. Spoilage in packaged poultry products is mainly due to the growth of microorganisms such as *Escherichia coli*, *Staphylococcus aureus*, *Campylobacter* sp., *Salmonella* sp., *Pseudomonas* sp., and *Listeria monocytogenes*. Furthermore, the growth of microorganisms can produce a variety of metabolites such as CO_2, NH_3, and H_2S during storage and negatively affect organoleptic characteristics and nutritional value of packaged poultry products. Thus, smart freshness indicator for the real-time evaluating of poultry product quality and safety is needed. Many studies have demonstrated the development of smart freshness indicator for monitoring poultry product quality and safety (Table 5.4).

5.5.3 Fish and Seafood Products

Fish and seafood products are highly susceptible to microbial and enzymatic deterioration, owing to their richness in protein nitrogenous substances, non-protein nitrogenous substances, polyunsaturated fatty acids, and other growth factors. A major characteristic in monitoring packaged fish and seafood products is freshness, which can be investigated by releasing TVB-N. During fish and seafood product spoilage, volatile amines, such as TMA, NH_3, and DMA, are generated by microorganisms and are responsible for the fishy odor and flavor. In general,

Table 5.3 Smart freshness indicators for monitoring meat product quality and safety

Meat products	Packaging/film materials	Dye indicator	Marker	Indication (color changes)	References
Lamb meat	Methylcellulose/chitosan nanofiber	Barberry anthocyanin	TVB-N	From pink to pale green and turned to yellow	Alizadeh-Sani et al. (2021)
Pork	Cellulose	Naphthoquinone dyes extracted from *Arnebia euchroma*	TVB-N	From magenta to purple	Dong et al. (2020)
Pork	Methylcellulose	Mixture of bromothymol blue and methyl red	TVB-N	From red to goldenrod and turned to green	Chen et al. (2019)
Pork	Starch/polyvinyl alcohol	Roselle anthocyanin	TVB-N	From red to green and turned to yellow	Zhang et al. (2019)
Pork	Polyvinyl alcohol/sodium carboxymethyl cellulose	Red cabbage anthocyanin	TVB-N	From red to blue-green	Liu et al. (2021)
Pork	Cellulose fibers	Bromothymol blue	TVB-N	From yellow to green	Cao et al. (2019a, b)
Pork	Agar/potato starch	Purple sweet potato anthocyanin	TVB-N	From red to green	Choi et al. (2017)
Pork	Chitosan/polyvinyl alcohol	Red cabbage anthocyanin	TVB-N	From translucently sea green to pink and turned to yellowish with pale green	Vo et al. (2019)
Beef	Cellulose acetate	Methyl red	TVB-N	From red to yellow	Lee and Shin (2019)
Beef	Filter paper	Methyl red Bromocresol purple	TVB-N	From red to yellow From yellow to purple	Kuswandi and Nurfawaidi (2017)
Beef	Pectin	Red cabbage extract	TVB-N	From purple to yellow	Dudnyk et al. (2018)
Minced beef	Cellulose–chitosan	Alizarin	TVB-N	From yellow to brown and turned to purple	Ezati et al. (2019a, b)

TVB-N total volatile basic nitrogen

increased levels of TVB-N are accompanied by increased pH in the packaged fish and seafood products as a result of bacterial metabolism. Moradi et al. (2019) developed smart freshness indicator from bacterial cellulose nanofibers incorporated with black carrot anthocyanin for monitoring the freshness of rainbow trout and

Table 5.4 Smart freshness indicators for monitoring poultry product quality and safety

Poultry products	Packaging/film materials	Dye indicator	Marker	Indication (color changes)	References
Chicken breast	Sugarcane bagasse nanocellulose	Bromothymol blue/ methyl red	CO_2	From green to red	Lu et al. (2020)
Chicken breast	Poly(ether-block-amide)	Alizarin Red S Bromocresol green Bromophenol blue Bromothymol blue m-Cresol purple Cresol red Curcumin Thymol blue	TVB-N and CO_2	From red to yellow From yellow to blue From yellow to blue No color change From red to yellow From red to yellow No color change From red to yellow	Lee et al. (2019)
Chicken breast	Chitosan/ polyethylene oxide	Curcumin	TVB-N	From bright yellow to red	Yildiz et al. (2021)
Chicken patties	Filter paper strips	Jamun fruit (*Syzygium cumini*) skin extract	TVB-N	From violet to yellow	Talukder et al. (2020)
Chicken	Cellulose fibers	Bromothymol blue	TVB-N	From yellow to green	Cao et al. (2019a, b)
Chicken	Agarose	Bromocresol purple	TVB-N	From light yellow to purple	Soni et al. (2018)
Chicken fillet	Pectin	Red cabbage extract	TVB-N	From purple to yellow	Dudnyk et al. (2018)
Chicken	Polyvinyl alcohol/gelatin	*Amaranthus* leaf extract	TVB-N	From red to yellow	Kanatt (2020)

CO_2 carbon dioxide, *TVB-N* total volatile basic nitrogen

common carp fillet during storage at 4 °C for 15 days. They reported that freshness indicator showed accurately sensed fish fillet spoilage by distinguishing color changes at different stages. During different freshness stages (fresh, best to eat, and spoiled), the indicator had deep carmine color, charm pink color, and jelly bean blue and khaki colors, respectively. Many studies have demonstrated the development of smart freshness indicator for monitoring fish and seafood product quality and safety (Table 5.5).

Table 5.5 Smart freshness indicators for monitoring fish and seafood product quality and safety

Fish and seafood products	Packaging/film materials	Dye indicator	Marker	Indication (color changes)	References
Fish (mud carp)	Gelatin/polyvinyl alcohol	Mulberry anthocyanin extracts	TVB-N	From purple to gray-purple and turned to dark green	Zeng et al. (2019)
Fish (grass crap)	Carboxymethyl cellulose/starch	Purple sweet potato anthocyanin	TVB-N	From pink to purple and turned to blue	Jiang et al. (2020)
Fish (Wuchang bream)	Agar	*Arnebia euchroma* root extracts	TVB-N	From pink to purple	Huang et al. (2019)
Fish (*Cyprinus carpio var. specularis*)	Sodium carboxymethyl starch/κ-carrageenan	Mulberry anthocyanin	TVB-N	From red to dark blue	Zhang et al. (2020)
Fish	Starch/polyvinyl alcohol	Mixture of curcumin and anthocyanin	TVB-N	From yellow to light yellow and turned to reddish brown	Chen et al. (2020)
Rainbow trout fillet	Starch/cellulose	Alizarin	TVB-N	From orange to reddish brown	Ezati et al. (2019a, b)
Rainbow trout and common carp fillet	Bacterial cellulose nanofibers	Black carrot anthocyanin	TVB-N	From deep carmine to charm pink and turned to jelly bean blue	Moradi et al. (2019)
Shrimp	Chitosan/polyvinyl alcohol	Anthocyanin from jambolan (*Syzygium cumini*) fruit	TVB-N	From red to blue	Merz et al. (2020)
Shrimp	Bacterial cellulose	*Echium amoenum* anthocyanin	TVB-N	From violet to gray and turned to yellow	Mohammadalinejhad et al. (2020)
Shrimp	Starch/polyvinyl alcohol	Red pitaya (*Hylocereus polyrhizus*) peel	TVB-N	From purple to yellow	Qin et al. (2020)
Shrimp	κ-Carrageenan	Curcumin	TVB-N	From yellow to red	Liu et al. (2018)
Shrimp	κ-Carrageenan	*Lycium ruthenicum* Murr.	TVB-N	From light gray to bluish green and turned to yellow	Liu et al. (2019)
Shrimp	Chitosan/polyvinyl alcohol	Cactus pears (*Opuntia ficusindica*) extract	TVB-N	From purple to orange and turned to yellow	Yao et al. (2020)

Shrimp	Polyvinyl alcohol/okra mucilage polysaccharide	Rose anthocyanin	TVB-N	From purple to blue to dark green and turned to yellow	Kang et al. (2020)
Shrimp	Cellulose fibers	Bromothymol blue	TVB-N	From light yellow to blue-green	Cao et al. (2019a)

TVB-N total volatile basic nitrogen

5.6 Conclusions

Because animal-based products are important source of nutrition for humans, they also play an important role in the economic growth. As a result, the new packaging technology has been continuously developed to meet consumer needs in the animal-based product area. Recently, the effective potential of smart freshness indicators based on natural biopolymer materials incorporated with natural dye indicators for the real-time monitoring of animal-based product quality and safety has been demonstrated by many studies. The developed smart freshness indicators have exhibited great sensitivity toward pH and target metabolites, showing color variations and thus exhibiting prospective use as visible smart freshness indicators. The use of smart freshness indicators could improve product quality and safety, and real-time monitoring and reduce food loss across the supply chain. However, smart freshness indicators also have many limitations, such as some dye indicator had broad-spectrum color changes and can be provided false-negative results, which lead to the producer rejection and consumer reliability. Therefore, the further development of extremely sensitive freshness indicators, more exact color, and cost effectiveness is of great significance for commercialization opportunity and increasing consumer acceptance.

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Packaging of Dairy Products: Emerging Strategies

6

Marta Biegańska

Abstract

Consumer demand for dairy products has changed significantly in recent years. Globalization, urbanization, and changing lifestyles with increasing number of consumers with higher incomes in developing countries keep pushing demand for innovative dairy products. The current trend observed on the dairy market regarding healthy products forces producers to increase the variety of premium and specialty products. Consumers are more aware nowadays of health benefits of dairy products and require controlled quality, convenience (e.g., on-the-go dairy), extended shelf life, and eco-friendly products. To meet these growing requirements, manufacturers are introducing product innovations to the market, as well as modern packaging. Beside the typical packaging functions like protection, containment, communication, marketing, and ergonomics novel packaging should also have an active role. As dairy products are highly perishable, they require proper packaging in order to protect and prolong shelf life of the product inside. Among different types of packaging, active and intelligent packaging is a powerful tool, alongside with novel packaging materials (e.g., paper-based, bioplastics). Moreover, novel packaging can be a tool for detecting food fraud, but also facilitates traceability. This review will cover potential use of smart packaging with indicators (e.g., gas/integrity, freshness, time-temperature), antimicrobial coatings, data carriers, sensors in dairy packaging.

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Dairy products · Shelf life · Smart packaging · Active packaging · Intelligent packaging · Data carriers · Sensors

6.1 Introduction

Packaging has been used from the moment when primitive man began to stockpile food. Over the years and with the development of civilization, it has become more and more sophisticated and complex. Packaging in the past and now is designed to fulfill specific functions, such as protection, containment, communication, marketing, and ergonomics. The primary function of any packaging is to protect the product from the surrounding environment. When it comes to food stuffs, it should be a barrier to temperature abuse, light, moisture changes, gases, pressure, odors, microorganism, pests, dirt, and dust (Ščetar et al. 2019; Alizadeh-Sani et al. 2019; Mirza Alizadeh et al. 2020; Elsherif et al. 2020). The second important function of any packaging is its communication. In recent years, packaging has become a major brand communication vehicle. From a consumers' point of view, it is the first point of contact with a particular brand—a so called "silent seller". In other words, packaging has become an important feature of brand differentiation and factor in consumers' purchase decisions (Omeni and Daniel 2020). However, this basic and also passive role of a packaging in modern, urbanized world is not enough. In this view, it mostly allows for protecting and preserving food helping to reduce food waste. Moreover, consumers are more aware of safety hazards related to food and demand safe, high quality and convenient products with extended shelf life (Sajdakowska et al. 2020; Chávez-Martínez et al. 2020). Food safety issues pose a significant challenge worldwide as foodborne illnesses result in productivity loss and increased treatment cost of $15 billion annually (e.g., hospitalization costs) (Sindi et al. 2020). As dairy products provide suitable conditions for the development of a number of microorganism, including pathogens, and because contamination of those products can occur at various production stages ensuring safety and prolonging shelf life are essential (Delorme et al. 2020).

Due to busy and more complex lifestyle, an on-the-go eating and drinking trend is visible even on the dairy market. Nowadays dairy packaging is very important as it is a vehicle for product differentiation, enables communication of the content, and is a powerful branding tool (Mania et al. 2018a; Velasco and Spence 2018; Šerešová and Kočí 2020).

In order to adapt to these changing trends and consumer expectations, the dairy market is forced to significantly increase the variety of products. This leads to increase of snack-sized, resealable, portion-controlled packaging. However, single-use packaging contributes to the increase in the amount of packaging waste (Šerešová and Kočí 2020). On the other hand, as dairy products are highly perishable, food waste and food loss in the food chain are also a problem. According to FAO as much as 1.3 billion tons of food are wasted globally each year, a 1/3 of the world production (Garnier et al. 2017; Bilska and Kołozyn-Krajewska 2019; Lipińska et al. 2019). This results in up to $1 trillion of economic losses annually. There is a difference between food loss and food waste. The first being loss occurring during production, postharvest treatment, and storage, whereas the latter is the food disposed of by retailers and consumers. To avoid or at least reduce food waste, the package should be convenient for its users. It ought to be easy to handle and refill without any mechanical damage to the product. Moreover, it should be easy to open, resealable, and allow for maximum emptying (Mania et al. 2018a). Packaging in its protection function can aid reduce food waste, but with novel packaging solutions it can also help to lower food losses along production and supply chains which are in line with the United Nations Sustainable Development goal to halve per capita global food waste (Wikström et al. 2019).

In recent years, consumers have shown rising health awareness that is anticipated to trigger some market trend, e.g., products with high protein content, lactose-free, sugar-free, nondairy alternatives or fortified and functional dairy. Those trends and growing market and consumer demand, due to changes in lifestyle and market globalization, have forced manufacturers to seek new packaging solutions like smart packaging (SP) (Mirza Alizadeh et al. 2020). The correlation between SP and main packaging functions, as well as different areas active and intelligent packaging cover is shown in Fig. 6.1.

Smart packaging combines the functions of both active and intelligent packaging. Both systems can work separately or synergistically as smart packaging technologies, as shown in Fig. 6.2.

Active packaging systems are developed with active components in the packaging (e.g., antimicrobial coatings, gas emitters or scavengers, moisture absorbers) in order to maintain or extend the product quality and shelf life, whereas *intelligent packaging* aims at monitoring the state and quality of the product and shares information on

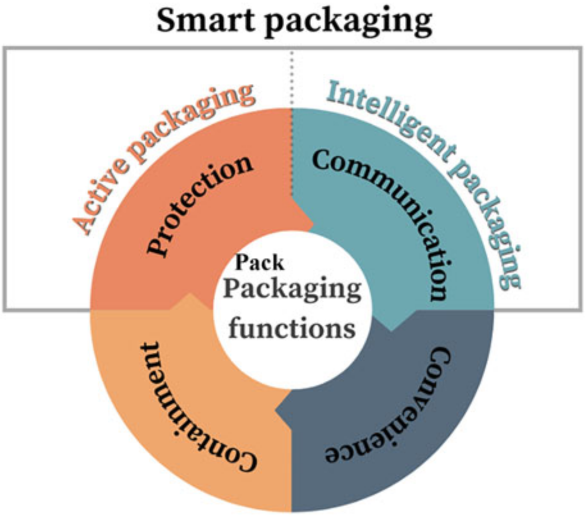

Fig. 6.1 Main packaging functions (Source: Own work)

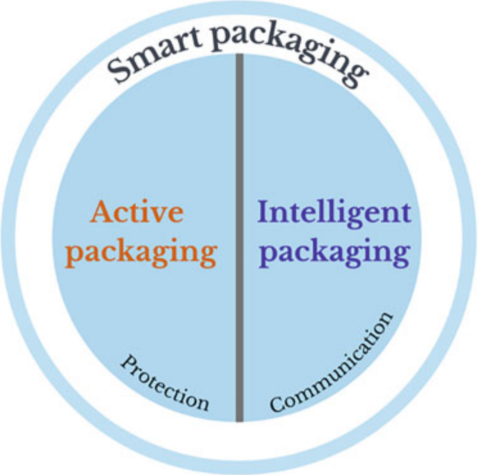

Fig. 6.2 Smart packaging (Source: Own work)

the storing and transportation conditions throughout the distribution chain (e.g., indicators, sensors, and data carriers) (Drago et al. 2020). They will be discussed in more detail further in the chapter.

Different packaging materials are being used nowadays depending on product type, processing and storing conditions, handling requirements, and way of use/consumption. Most often used are: glass and plastic bottles, multilayer materials (e.g., Tetra Pak®, SIG Combibloc), pouches, plastic trays, cans, tubs, and buckets. They have to meet some requirements like to be printable, safe for food contact, inert, not to interact with the packed product (except for active packaging), nontoxic, be compatible with the product, show appropriate impact resistance, have barrier properties toward light, gases, and odor, have the right shape and size, be cost-effective, and have marketing appeal (Ščetar et al. 2019).

6.2 Dairy Market Overview

Healthy eating habits include consumption of a wide variety of products of high nutritional density. High-quality protein, minerals, and group B vitamins can be found in milk and dairy products. These are essential in the diet of children, pregnant women, and the elderly (Owusu-Kwarteng et al. 2020; Delorme et al. 2020; Smirnova et al. 2020; Tricarico et al. 2020; Chávez-Martínez et al. 2020).

Global dairy market is estimated at over $400 billion worth, which is circa 14% of worldwide agricultural trade, where milk is the third agri-food commodity (Tan and Ngan 2020).

As dairy products are made from raw milk (cow, sheep, goat, buffalo, camel, and other milking animals), it shows differences in composition due to seasonal fluctuations, origin or rearing (Faccia et al. 2020). Commercially available milk comes in different types such as ultra-high-temperature (UHT) milk, pasteurized

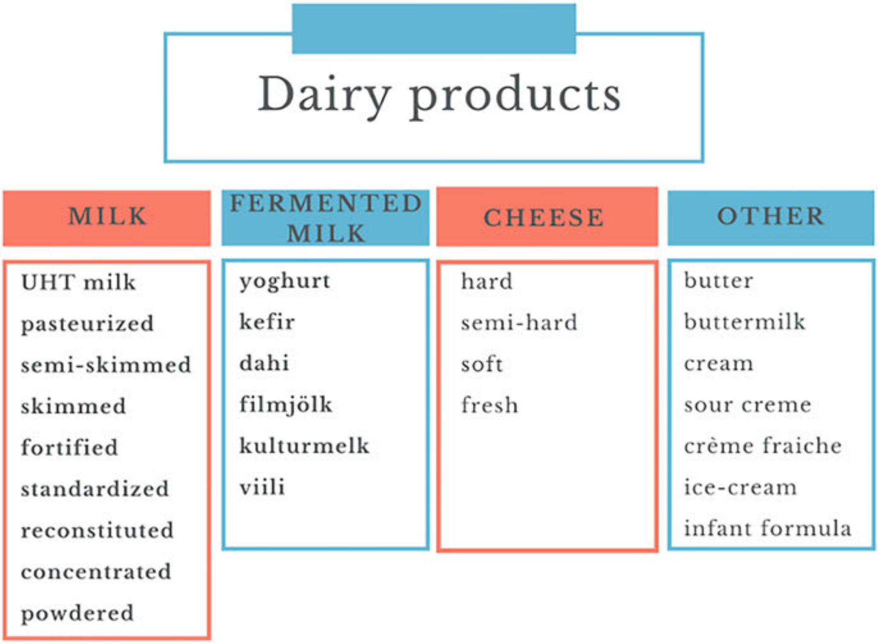

Fig. 6.3 An overview of dairy products (Source: Based on (Najib et al. 2020; Byberg and Lemming 2020)

milk, semiskimmed milk, skimmed milk, fortified milk, standardized milk, and reconstituted milk (Byberg and Lemming 2020; Faccia 2020a). An overview of dairy products is shown in the Fig. 6.3.

Milk contains important micronutrients and for this reason is regarded as an important part of a balanced diet. However, in its raw state, it is highly susceptible to microbial and enzymatic spoilage (Odueke et al. 2016; Smirnova et al. 2020).

One of dairy products is kefir; it can be made from different types of milk, like cow, goat, sheep, buffalo or camel during microbial fermentation. Kefir has an acidic taste, contains many bacterial species known for their probiotic properties, and is creamy. During storage, its sensory and microbial properties can still change improving its shelf life. It has many health benefits and exhibits antimicrobial activity, due to presence of lactic acid bacteria (LAB) capable of producing bacteriocins, against for example *S. aureus, E. coli*, *Salmonella enteritidis*, *B. cereus,* and *L. monocytogenes* (Sindi et al. 2020). Most common genera of LAB are *Lactobacillus* and *Bifidobacterium*. They owe their biological functions to bioactive metabolites and among health benefits anticarcinogenic, antiobesity, antioxidant effect, and stimulation of immune response need to be mentioned (Mohamed et al. 2020). Nevertheless, it has short shelf life and high storage and packaging costs which have led to the trend of having dry kefir in powder form (through freeze or spray drying) (Farag et al. 2020).

Another most often consumed worldwide nutritious and healthy product is yoghurt (Sajdakowska et al. 2020). It is a fermented dairy product originating in the Balkans and the Middle East. Its shelf life is usually 3 weeks or less. Thanks to presence of lactic acid bacteria, it has a probiotic effect (Odueke et al. 2016). Lactic acid bacteria LAB are essential in production of fermented dairy products. The quality of fermented product depends on the bacterial strain used in the process (Mohamed et al. 2020). There are several types of yoghurts that gain in popularity like drinkable yoghurt, spoonable, Greek-style yoghurt (Newbold and Koppel 2018).

Cheese is one of the most important dairy products that come in many varieties (e.g., flavor, texture, size, and origin). It undergoes many changes (e.g., microbial, biochemical) during production and ripening. The manufacturing of cheese is one of the oldest technologies for prolonged milk nutrients consumption. It is most often classified as hard, semihard, soft, and fresh. Although, fresh cheeses are considered to be soft cheeses due to their high moisture content and fairly short shelf life (Youssef et al. 2017). Cheese comes in three main types: natural cheese, powdered cheese, and processed (melted analog) cheese. Natural cheese is prepared from pasteurized milk and its aging continues "on the shelf". Taking that into account, it requires packaging with high barrier properties. Powdered cheese used mainly for snack foods flavoring is produced by dehydration of natural cheese. Finally, processed cheese is manufactured by melting natural cheese with additives (e.g., water, salt, whey, emulsifiers) to prolong its shelf life (Mania et al. 2018a).

6.3 Dairy Product Portfolios and Changing Market Demands

Milk and dairy supply chains play a significant role in world food demand. The growing world population and the increase in wealth of people in developing countries have a significant impact on this demand. On the other hand, markets in developed countries seek nutritionally balanced and environmentally sustainable products forcing manufacturers to develop product innovations such as functional products (Faccia 2020b). Dairy supply chains are complex and difficult to model due to high variability of raw materials supply, large variety of products, their perishability, and changing demand. A simplified logistic chain is shown in Fig. 6.4. As dairy products, especially milk and its by-products, demonstrate high nutritional value; the use of fortifying additives to increase that value was only a matter of time (Guarnaschelli et al. 2020).

Traditional milk preservation methods include among others pasteurization, ultra-high-temperature, and sterilization. Table 6.1 presents heat treatment methods in the dairy industry. Traditional dairy preservation techniques are applied to inhibit microbial growth, increase shelf life, and maintain quality and safety. However, they can alter organoleptic properties and decrease levels of nutrients. To avoid these adverse effects, emerging technologies such as high hydrostatic pressure (HHP), pulsed electric fields (PEFs), ultrasound (US), irradiation, and cold plasma (CP) are gaining more attention. Irradiation as a nonthermal technology for food preservation

Fig. 6.4 A simplified dairy logistic chain (Source: Based on (Guarnaschelli et al. 2020))

Table 6.1 Heat treatment methods in the dairy industry

Heat treatment	Temperature [°C]	Time	Product
Thermization	57–68	5 s–30 min	Raw milk Some cheeses
Pasteurization	72–80	15–30 s	Drinking milk Cheese
Pasteurized with extended shelf life (ESL)	125–140	1–10 s	Drinking milk with ESL at chilled conditions
Ultra-high-temperature (UHT)	135–150	1–10 s	Drinking milk with long shelf life at ambient temperature
In-container sterilization	110–120 125	10–20 min 5 min	Condensed milk, drinking milk with long shelf life at ambient temperature
	90–95	5–10 min	Yoghurt
	72–80	15–30 s	Low-heat skim milk powder (SMP)
	85 90 105	1 min 30 s 30 s	Medium-heat SMP Preheating in UHT Whole milk powder
	90 120 135	5 min 1 min 30 s	High-heat SMP
	>120	>40 s	High-high-heat or high-high-heat-stable SMP

Source: Based on (International Dairy Federation 2018)

has been utilized for many years and acknowledged by World Health Organization (WHO) as beneficial for the provision of quality, ensuring safety and extending shelf life. Irradiation at low doses and/or in frozen conditions can be effective in pathogens elimination without off-flavors in the irradiated product (Odueke et al. 2016). Another promising innovative technology with commercialization potential is ultraviolet (UV) radiation that has shown effectiveness on microbial safety and intrinsic quality properties of dairy products (Delorme et al. 2020).

UV light comprises the wavelengths range from 100 to 400 nm in which four types of rays can be distinguished: UVA (315–400 nm), UVB (280–315 nm), UVC (200–280 nm), and vacuum-UV (100–200 nm). Among those types, UVC rays are known for their microbial elimination (e.g., bacteria, viruses, and fungi). However, further studies are needed to optimize conditions of UV treatment of dairy products to overcome modifications of physicochemical and sensory features (Delorme et al. 2020).

Increasingly diverse consumers' needs regarding dairy products lead to changing production patterns in the dairy industry. They can be described as mass customization as manufacturers offer a wide variety of products meant for different consumers with different needs and expectations. Products attributes regarded as most important by consumers in relevance to ice-cream were taste, appearance, shape, texture, health benefits, and packaging material (Wedowati et al. 2020). Although those results were related to ice cream, but to a large extent they may also apply to other dairy products.

6.3.1 Functional Dairy Products

Fortification traditional dairy products with active ingredients lead to functional dairy products with enhanced nutritional value and even improved health benefits. Functional food market has grown significantly in the last couple of decades, mostly because of use of prebiotics and probiotics (Lai et al. 2020; Faccia 2020b). Functional dairy products include:

- Low-fat dairy
- Lactose-free dairy
- Products fortified with added functional ingredients (Lai et al. 2020)

For example, addition of Chinese sweet tea extract (*Rubus suavissimus* S. Lee leaves) to buffalo milk yoghurt improved the biological activity of the product (antioxidation and antihypertensive). Another study showed that fortification of buffalo milk yoghurt with fenugreek (*Trigonella foenum-graecum*) and *Moringa oleifera* seed flour leads to modification of mineral compounds and showed higher antibacterial activity against some undesired species, compared to unfortified yoghurt (Faccia 2020b). Lai et al. (2020) reported that fortification of yoghurt with algal oil (25% of fat content) to increase omega-3 fatty acids content did not seem to cause an off-flavor. Moreover, addition of inulin acting as a prebiotic for the increase of probiotic gut bacteria is another fortification example, just like the fortification with whey protein in sheep and goat milk dairy products. Fortification may take the form of additives constituting by-products from other food industries like vegetable, fruit, marine or cereal. A wide range of examples were presented by Iriondo-Dehond et al. (2018) among which authors mentioned fruit skin, peels, leaves, and pulp or bran cereals and fish oil.

In order to lower fat content in yoghurts, fat replacers are used. Different types of starch (e.g., corn, sweet potato, potato, chickpea, and Turkish beans) can serve as fat lowering agents. Moreover, functional additives can also be added to other dairy products such as cheese. Faccia (2020b) studied kiwi juice as cheese coagulant and although, longer coagulation and syneresis were observed, compared to calf rennet, investigated cheese exhibited higher concentrations of polyphenols and phytosterols. Crockett (2015) studied Allanblackia oil as a potential functional additive. It demonstrates good storage stability characteristics and relatively high melting point which make it a promising consistency improving agent in butter substitutes and vegetable-based dairy products.

People suffering from lactose intolerance exhibit decrease in enzyme (-β-galactosidase) production that is responsible for lactose hydrolyzation. This in turn leads to gut digestion of lactose which shows unpleasant symptoms like abdominal cramps, flatulence, and diarrhea. Around 75% of adult global population suffers from enzyme decrease. Such state leads to increased lactose-free dairy demand. However, milk from sheep and goat seems to be better tolerable by lactose-intolerant consumers, there is a trend in removing lactose from this type of milk as well like in lactose-free Ricotta cheese (Lai et al. 2020). There are also products that contain little or no lactose like Gouda, Parmesan, Cheddar, Swiss cheese or butter. Fresh cheese, however, can contain lactose at levels resulting in reaction among lactose-intolerant consumers.

Among market-available lactose-free products are potable milk, UHT milk, yoghurts, cheese, ice-cream, flavored milk, dairy powders, creams, desserts, and Dulce de Leche (Dekker et al. 2019).

6.3.1.1 Nanoceuticals

Addition of nutraceuticals like carotenoids or lycopene, omega-3 fatty acids, minerals, vitamin D_2, phytosterols, and some probiotic bacteria species to conventional dairy products can improve their bioavailability. They are also generally recognized as safe (GRAS) by the Food and Drug Administration (FDA). They can be incorporated into the products in a form of nanoclusters, nanocages, and nanodrops. Compared to fortification described above, the main difference is in the size of the bioactive compound ranging from 1 to 100 nm in length. These nanoscale compounds show better solubility, biological activity, and bioavailability. They are also more stable during heat processing and storage to normal-size nutraceuticals (Kuswandi 2017; Poonia 2019).

Encapsulated edible nanoparticles containing drugs, vitamins, micronutrients incorporated into the packaging surface could deliver those particles through controlled release in the human body at targeted organs and improve health (Kuswandi 2016; Singh et al. 2019).

6.3.1.2 Novel Fermented Dairy Products

Although, probiotic bacteria (LAB) are already known in kefir and yoghurt, the increased popularity of the probiotic concept having benefits to human health. For this reason, an emerging trend to use them in other dairy products such as cheese, dairy desserts, and ice cream can be detected. Changing dietary patterns have led to creation of a market niche for probiotic foods (Ávila et al. 2020). Addition of herb extracts, fresh spices or fruit fibers to yoghurts can increase the phytochemicals content and health benefits. Dimitrellou et al. (2020) investigated yoghurts supplemented with aronia, blueberry, and grape juices to increase the amount of phenolic compounds and antioxidant activity. Addition of investigated juices increase red color of prepared yoghurts, but had no significant effect on physico-chemical properties.

6.3.2 Products Beyond Dairy

Going beyond dairy is another emerging trend on the market. According to Stora Enso *Gainomaxs'* sports nutrition, UHT drinks are displayed together with other sports nutrition products outside dairy shelf (Stora Enso n.d.). Another example is Credition Dairy's (Devon, UK) brand *Arctic Coffee* that comes in several flavors and carton sizes of 330 mL and 1 L and gives consumers the experience of on-the-go coffee with milk (Elopak 2020).

One of possibilities is the use of dairy products in making functional bakery products. Graça et al. (2019) studied the addition of yoghurt and curd cheese to wheat bread to enhance its functional and nutritional value. As dairy products can help increase the amount of minerals like Ca and P, vitamin A and B12, as well as protein and essential amino acids. Research showed that yoghurt addition had a positive effect on the rheology of the dough. Both breads obtained good sensorial acceptability with yoghurt and curd cheese additions of 50 g and 30 g, respectively.

6.3.2.1 Plant-Based Dairy Alternatives

Dairy alternatives are made from plant-based milk instead of animal milk. With growing consumer demand, more and more such products are available on the market. The reasons behind this trend are both health and sustainability. Global dairy alternative market is estimated to grow to 20% of the value of the dairy milk market in 2021. Among plant-based alternatives are soy-based drinks, almond-based drinks, oat-based drinks, rice-based drinks, tofu spreads (Jeske et al. 2018; Leialohilani and de Boer 2020; Paul et al. 2020). In 2020, Arla has launched a range of dairy-free plant-based drinks in Denmark under the brand name Jörd made from oats, barley, and hemp (Elopak 2020).

6.4 Dairy Packaging Innovations

Development of dairy packaging is a result of advances in material technologies and consumer demands. Commonly used materials include:

- Glass [inert, recyclable, impermeable to gases and water vapor, brittle, heavy in weight; bottles and jars]

- Metal [recyclable, rigid, gas barrier properties, requires coatings to prevent corrosion; cans or thin film wrappings]
- Paper/cardboard [recyclable, biodegradable, light in weight, printable, permeability for breezing, water vapor and oxygen, susceptible to tearing; secondary packaging, e.g., boxes, wrappings]
- Waxed papers [good resistance, good heat-sealing characteristics, low-cost, moisture barrier properties]
- Poly(vinylidene chloride) (PVDC) [gas, water vapor, fatty and oil products barrier properties, used in MAP]
- Cellophane [clear films, used in coatings and laminates, poor strength properties]
- Low-density polyethylene (LDPE, LD-PE, PELD, PE-LD) [recyclable, low-cost, flexible, moisture barrier properties, resistant to most solvents, low gas barrier properties; cups, trays, tubs]
- High-density polyethylene (HDPE, HD-PE, PEHD, PE-HD) [recyclable, low-cost, moderately flexible, odorless, poor clarity, low oxygen and other gases barrier properties; cups, trays, tubs]
- Poly(vinyl chloride) (PVC) [use of plasticizers, low moisture barrier properties]
- Multilayer packaging (plastic/paperboard/aluminum) [aseptic, moisture, gas, odor, light barrier properties; pouches, sachets, cartons, bottles] (Roohi et al. 2018; Ščetar et al. 2019)

Packaging manufacturers keep on developing their products to fulfill growing market and consumer demand. Ampacet (NY, USA) has launched their sustainable 3R solutions (Reuse, Reduce, and Recycle) to help meet sustainability goals. To give an example Ampacet's Safari White PET masterbatch offers high level of opacity and reduced mineral loading of less than 4%. It is suitable for ultra-high temperature (UHT) processed milk which has an unrefrigerated shelf life of 6–9 months. Safari PET preserves flavor and nutrients of fresh milk and protects it from light exposure in 400–550 nm wavelength (Anonymous 2019).

Wipak (Helsinki, Finland) offers monomaterial film BIAXOP ECO 70 XX XPP which is recyclable and has excellent transparency, with an integrated barrier layer for an even better level of product protection and tight seal. When an easy-open PEEL-solution for lidding filmsand flow packs is required, BIAXEN ECO 65 XX XFP offers a wide sealing window and early sealing initiation temperature. Polyolefin-based resealable lidding REPAK® TOP BP 70 XX and PE-based bottom NICE ECO XX 17 are also recyclable. Wipak has also launched rPET with a high recycled content in the semirigid MULTICLEAR-R 250 bottom film with great optical and mechanical properties. With high-quality recycled PET granulate, the solution allows for a high carbon footprint reduction and the material is fully approved by the European Food Safety Authority (EFSA) for use as a food contact material. In the area of renewable materials are PAPER TOP® PD BE 90 XX PEEL lidding film and PAPER BTM® Q 330 XX bottom film. Wipak’s PAPER BTM® range, provides different solutions with up to 90% paper share, all enable consumers to separate film and paper before disposal (Wipak 2021).

Danish organic cooperative dairy Naturmælk has introduced its vast range of milk, yoghurt, buttermilk, and cream varieties in Pure-Pak® cartons with Natural Brown Board, and Mini Pure-Pak® cartons from Elopak (Oslo, Norway). Moreover, new Pure-Pak®Imagine carton is even more environmentally friendly than other cartons as it has 10 times less plastic compared to PET bottle and 46% less plastic than a carton with a closure. Pure-Pak®Imagine is designed with an easy-pour opening with an easy-fold feature, no plastic screw cap, and is 100% based on wood. This type of closure also provides maximum emptying capabilities of the carton minimizing food waste. It has a unique top fin-guiding consumer on how to open the carton and form an easy-pour spout which is similar to carton openings in the 70s and 80s (Elopak 2020).

Sustainability and environment awareness of consumers force packaging development. Another example is Chadwicks' (Greater Manchester, UK) paper-based lids for dairy products. Those lids are fully recyclable, offer good barrier properties (oxygen, water vapor, aromas), and high mechanical strength and stiffness. They are also printable and show excellent optical properties. Those paper-based lids consist of polyethylene-coated paper with linen or pin dot emboss. The embossing includes print, paper, and coextruded barrier polymer (Chadwicks 2021).

Among novel packaging systems, modified atmosphere packaging (MAP), edible cheese packaging or biodegradable packaging should be mentioned which will be described in more detail in this chapter.

6.4.1 MAP Packaging

Modified atmosphere packaging (MAP) has been previously used for fruit and vegetables, meat fish, and bakery products. This technology is based on altering the gaseous combination inside the packaging to extend product's shelf life. This is obtained by using specially composed gas mixtures of carbon dioxide, oxygen, and nitrogen. This approach allows for decreased microbial growth and reduction of lipids oxidation, thus prolonging shelf life and quality of dairy products. Lipid oxidation is responsible for quality deterioration in dairy products as oxidation of unsaturated fatty acids results in the formation of chemical compounds that give off-flavors and affect shelf life and storage stability (Clarke et al. 2020). Addition of CO_2 to a gas barrier packaging allowed for extending shelf life of cottage cheese of 200–400% (Newbold and Koppel 2018). This technology can be applied with success to prolong shelf life of soft cheese, semihard cheese, hard cheese, cottage cheese, whey cheese, fresh cheese, and surface mold-ripened cheese. Depending on the cheese type in order to inhibit the growth of anaerobic microorganism, CO_2 concentrations inside the packaging ought to vary between 20 and 60%. Usually to minimize lipids oxidation processes in MAP of dairy products, the level of O_2 should be as low as possible. In this case, combinations of CO_2 and N_2 should be 30/70, 40/60, 60/40, 50/50 accordingly. Although, this method allows for extending shelf life of cheeses before choosing the right gas ratio cheese type, production process and packaging material need to be considered (Garnier et al. 2017; Ščetar et al. 2019).

6.4.2 Edible Coatings

To meet consumer acceptability and satisfaction, cheese requires an adequate packaging to protect its quality, and safety films and coatings have been used for a long time. Covering cheese methods before ripening or during storage can prolong shelf life and minimize defects in the finished product. Consumer preferences regarding appearance and sensory features of cheese make the selection of packaging and coating an important factor in buying decisions. Moreover, environmental awareness and sustainability are also forcing manufacturers to seek recyclable or biodegradable packaging materials to minimize package waste. In recent years, there has been a growing interest in edible film and coating in the dairy sector. Edible coatings/films are thin layers of food biopolymer-based material for covering food, like cheese. Films are prepared separately and applied in the form of a wrapping material, whereas coatings are suspensions or emulsions applied directly and forming a film on the surface of cheese. Some polysaccharides, lipids, and proteins have been used as edible cheese coatings (with or without plasticizers, antimicrobial agents, and nanoparticles) to prolong shelf life (Table 6.2). Application of a film or coating can protect cheese from moisture losses, gas exchange, microbial and chemical deterioration, and physical damage. Traditionally waxes have been used as cheese coatings; however, a combination of waxes with emulsions based on polysaccharides and proteins may lead to the formation of a new generation of edible coatings (Youssef et al. 2017).

Alizadeh-Sani et al. (2019) studied storage stability of corn starch-based edible films as a wrapping of milk cake. It is a product prepared directly from milk or from a granular variety of *khoa*. During storage, it is susceptible to oxidative rancidity and absorbs odors from its surrounding environment. Traditionally milk cake is wrapped in butter paper and placed in paperboard secondary packaging. Compared to control, starch-based films demonstrated slower decrease in sensory scores under refrigerated conditions. They exhibited storage stability of 18 days without signs of spoilage. The films thickness, water activity, moisture, water solubility, and water vapor transmission rate were significantly increase, but mechanical properties and transmittance decreased with storage period.

6.4.3 Biodegradable Packaging

Biodegradable food packaging materials are films that after use decompose with the help of microorganisms through composting where they are degraded into CO_2, water, methane, and biomass. Different microorganisms use such biodegradable materials as carbon source. The biodegradation leads either to disintegration of the polymer or its fragmentation without harmful effect on the environment. They are obtained from renewable, abundant, and low-cost materials and can be alternative food packaging materials (Roohi et al. 2018; Adeyeye et al. 2019; Kuswandi and Moradi 2019). Those “natural polymers” or biopolymers are mainly of microorganisms’ origin and are in nature carbohydrates. They create hydrophilic

Table 6.2 Edible coating materials in dairy industry

Material/additive	Compound	Properties	Product
Biopolymers	Chitosan	• Nontoxic • Biodegradable • Forms strong flexible films • Shows antimicrobial activity	• Fior di latte cheese • Ricotta cheese • Ras cheese • Saloio semihard cheese
	Galactomannans	• Controlled gas transfer • Structural stability • Low moisture retention • Freeze-thaw stable (cold water soluble gums)	
	Alginates	• Sodium alginate forms a fairly strong film	• Mozzarella • Fior di latte cheese
	Carrageenans	• Have different solubility in water (depending on the degree of sulfation: δ, ι, κ) • Show similar puncture force • κ gives strongest film among all three types	
	Carboxy methyl cellulose (CMC)	• Forms films with different strength (depending on molecular weight and degree of substitution) • Film strength is lower compared to ones from alginates at similar concentrations	
	Starch and derivatives	• Can create clear and flexible coatings when modified • Addition of plasticizers improves film properties, but reduces barrier characteristics	
	Proteins (e.g., whey proteins, and zein)	• Good mechanical stability • Excellent gas and lipid barrier properties • Poor water resistance • Susceptibility to cracking	
Plasticizers	Glycerol, sorbitol, ethylene glycol	• Improve the elastic modulus and mechanical properties of films • Increase in resistance to permeation of vapors and gases	
Surfactants and lipids	ND	• Improve the emulsions stability • In coatings reduce surface tension and improve wettability	

(continued)

Table 6.2 (continued)

Material/additive	Compound	Properties	Product
Antimicrobial agents Nanoparticles Bionanocomposites	Organic acids and their salts – Sorbates – Benzoates – Propionates – Lysozyme Bacteriocins – Nisin – Natamycin – Primaricin Essential oils Silver (silver zeolite) Silver-montmorillonite – Embedded into agar – Used in MAP – Dipped in sodium alginate and immersed in calcium chloride – Chitosan/poly (vinyl alcohol)/ titanium nanoparticles – Chitosan/CMC/ zinc nanoparticles	• Antimicrobial agents against Gram(+) and Gram(−) microorganisms • Antimicrobial agent against Gram(−) microorganisms • Antifungal agent • Show wide spectrum effects on harmful microorganisms • Reduces significantly the number of viable *E. coli*, *S. aureus,* and *A. niger* after 30 min of application • Antimicrobial activity against three strains of Pseudomonas spp. • Showed shelf life extension above 5 days • Enhanced shelf life up to 10 days • Good mechanical and antimicrobial properties • Good mechanical properties • Good antimicrobial activity against S. aureus, *P. aeruginosa*, *E. coli,* and *C. albicans*	• Gorgonzola • Mozzarella • Fior di latte cheese • Fior di latte cheese • White soft cheese

Source: Based on (Youssef et al. 2017; Adeyeye et al. 2019)

films with good barrier properties to O_2, CO_2, and lipids. However, some biopolymers' performance is not yet comparable with traditional plastic materials. They are brittle and exhibit poor gas and vapor barrier properties. These drawbacks could be overcome through the use of nanomaterials (Adeyeye et al. 2019).

Starch-based packaging materials are biodegradable and with the use of plasticizers (e.g., glycerol, polyethers, and urea) can create films with appropriate for food packaging mechanical strength like tensile strength, high elongation. It can also be extruded and formed as thermoplastic materials and by using water steam it can be converted into foam, just like polystyrene (PS) packaging. Among advantages of starch in edible films are preparation simplicity, low-cost, good barrier properties to lipids and oxygen. Its drawbacks are poor water resistance and brittleness (Roohi et al. 2018; Adeyeye et al. 2019; Kuswandi and Moradi 2019).

Chitosan is a biopolymer with antimicrobial properties, is insoluble in water and soluble in acid solutions, and it also shows poor gas and water vapor barrier properties. Chitosan is a nontoxic, biodegradable, biocompatible packaging material (Adeyeye et al. 2019). It is mostly obtained from shrimp shells, fungi, yeast or green microalgae (Irkin and Esmer 2015).

Curdlan is yet another polysaccharide with excellent film-forming ability, abundant, nontoxic, and biodegradable. It is also water insoluble and demonstrates great thermal characteristics which could be incorporated in multilayer packaging materials (Adeyeye et al. 2019; Alizadeh-Sani et al. 2019).

Among biodegradable packaging materials are also ones produced *using traditional chemical synthesis* like polylactic acid (PLA), polyhydroxybutyrate (PHB), and polycaprolactone. PLA is made from renewable resources (sugarcane, corn) and has biocompatible and biodegradable properties. It requires chemical modification to improve its mechanical and physical properties. Despite that, it has the potential to be produced on a large scale and become an eco-friendly packaging material. PHB is created by microorganism and is compatible to dairy products, meat, and beverages. It is an excellent for food packaging films. Moreover, it is nontoxic, water insoluble, and shows better physical characteristics as food packaging material compared to polypropylene. However, due to its high degree of crystallinity, high melting temperature is brittle. Both of those described above polymers can be used in cheese or curdled milk packaging (Roohi et al. 2018; Adeyeye et al. 2019).

Microbial gums are nontoxic and have the potential to be produced on an industrial scale. As packaging materials, they are used to make gels, thickening agents, and film solutions. FDA recognized xanthan gum as food additive in 1969. It is an anionic, water-soluble polymer, and is stable at a wide pH and temperature range. Gellan gum is a suitable hydrocolloid for making edible films that are transparent and show good mechanical properties. Pullan has the ability to form colorless, transparent, odorless, and highly water permeable films. It is not used extensively in the packaging industry because of its high cost; however, polysaccharide blends with, e.g., alginate, chitosan, and starch create films easily dissolved in water. This could be utilized in development of edible food coatings with resistance to oxygen permeation (Alizadeh-Sani et al. 2019).

Protein-based packaging materials are also biodegradable, low-cost, and abundant. For example, whey, a cheese-making by-product can be filtered and dried to obtain pure whey protein, which can be then used to create protein-based films. Such films can be used for layered plastic films that could form packaging materials in a combination with recyclable plastics. After use, those layers can be chemically separated and plastics recycled (Kuswandi and Moradi 2019). Another protein with film-forming properties is gelatin. It is water soluble, odorless, tasteless, colorless, and transparent and is obtained through partial collagen hydrolysis in powdered or granulated form (Ramos et al. 2016). Due to its water solubility and swelling in contact with high moisture products, it needs to be modified prior to use in dairy applications.

The use of biodegradable materials in food packaging would reduce greenhouse gas emissions and increase the use of renewable sources of raw materials for their production (Sanyang and Sapuan 2015). However, at present, the production of this type of packaging on an industrial scale is insufficient due to insufficient facility of production (Roohi et al. 2018).

6.4.4 Biomaterials

Biochemically improved packaging materials are eco-friendly, but they do not necessarily have to be biodegradable as well. These bio-based materials use renewable resources as raw materials to decrease the use of traditional fossil fuels such as crude oil. They are in general nonrecyclable materials, but can be incinerated for energy recovery. As polyethylene terephthalate (PET) is a widely used petroleum-based food packaging material, it can be produced with the use of renewable resources giving rPET. Other examples of bio-based polyesters include:

- Polyethylene furanoate (PEF)
- Polytrimetylenefurandicarboxylate (PTF)

Both of them show improved barrier properties and higher mechanical strength (Kuswandi and Moradi 2019).

6.4.5 Nanomaterials

Use of nanoparticles in changing packaging materials characteristic and developing new materials was the result of market demand for packaging assisting in extending shelf life. Nano-based films can have improved barrier properties (e.g., CO_2, O_2, ethylene, moisture, lipids) which play a significant role in protecting food products from oxidation and spoilage (Poonia 2019). Nano-reinforced traditional polymers used in food packaging usually contain up to 5% w/w nanoparticles (Davarcioglu 2017; Pereda et al. 2018). Moreover, nanoparticles in the polymer matrix of common packaging materials increase physical properties of those materials such as strength, heat resistance, stiffness, shatterproof, and dimensional stability. In order to improve those properties, metal oxides, nanoparticles, nanoclays, carbon nanotubes, and metallic nanoparticles are used. Nanocomposites with nanoclays and layered silicates have improved diffusion paths (tortuous pathways) which in turn increase their barrier properties. However, many advantages of nanoparticles in plastic packaging have been shown in many studies and their main drawback is the polymer transparency reduction (Kuswandi and Moradi 2019). Amjadi et al. (2019) studied gelatin-based nanocomposite-containing chitosan nanofiber and ZnO nanoparticles as potential cheese wrappings. They showed significant decrease in pathogenic bacteria growth (*E. coli*, *S. aureus*, and *P. aeruginosa*). Prepared films did not alter the organoleptic properties of cheese until the end of storage that lasted 12 days.

6.5 Active Packaging for Dairy Products

The passive packaging function – protection – has been changed into an active one with the development and application of active packaging. They can take a form active component incorporated in the packaging material or labels, pads, sachets, and other forms to actively alter the conditions inside the packaging. Among active packaging solutions are gas scavengers or emitters, gas absorbers, antimicrobial agents, moisture control agents, antisticking films, and light absorbers (Jafarizadeh-Malmiri et al. 2019; Ščetar et al. 2019; Kuswandi and Moradi 2019). Carbon dioxide scavengers with iron oxide, calcium hydroxide, and activated charcoal in a form of sachets or films can be used in cheese packaging. Also flavor or odor absorbers such as cellulose triacetate, citric acid, ascorbate, clays, zeolites, activated carbon films enable smell and taste preservation, off-odors removal in dairy products (Vigneshwaran et al. 2019).

6.5.1 Active Coatings

Preparation of active coatings requires incorporation of active agents into polymer matrix (e.g., PE, PP, LDPE, PET, PS, and PLA) through embedding, immobilization or layer-by-layer deposition techniques. Such coatings can be either migratory or nonmigratory. In migratory active coatings, active substances are meant to migrate to the products for their specific function, e.g., antimicrobial, antioxidant, biocatalytic, nutraceutical (Irkin and Esmer 2015).

6.5.1.1 Enzymatic Coatings

The use of enzymes in active packaging solutions is predominantly used to control the growth of spoilage and/or pathogenic microorganisms. These substances can be incorporated into coatings by embedding and blending. Depending on the preparation technique of such active coatings (covalent immobilization, layer-by-layer deposition, and photografting), they can form migratory or nonmigratory materials. An LDPE film with glucose oxidase and catalase showed up to 97% activity even after exposure to 325 °C and remained its oxygen scavenging properties (Bastarrachea et al. 2015).

Agrillo et al. (2019) studied the antimicrobial effect of activated PET. The activation with small synthetic peptides resulted in the growth inhibition of aerobic plate count within first 24 h and was also effective against *L. monocytogenes* biofilm formation. Also enzymes can act as antimicrobial agents and be applied to different solid materials by means of immobilization. Mirabelli et al. (2018) used hen egg white lysozyme and immobilized it in crystalline form on hydrogel composite membranes (HCMs) to develop an antimicrobial biofilm. The enzyme was crystallized by using HCMs made of poly(vinyl acetate) (PVA) and poly(ethylene glycol) diglycidyl ether (PEGDE) as cross-linker and polypropylene membranes sheets. Lysozyme immobilized on PVA-HCMs in the molecular form demonstrated antimicrobial properties against *Micrococcus lysodeikticus* within 90-min incubation.

6.5.1.2 Antimicrobial Nanocoatings

Intensely studied is antimicrobial packaging using such agents as essential oils, organic acids, peptides, enzymes or biopolymers (Bastarrachea et al. 2015). The reason for this is that bacterial contamination can unfavorably affect the quality, safety, and shelf life of milk and other dairy products. The chemical composition of dairy products makes them an ideal medium for microbial growth (Hutchings et al. 2020). These antimicrobial agents such as nanoparticles of silver, magnesium oxide, copper oxide, titanium dioxide or carbon nanotubes can be coated, laminated, incorporated or immobilized onto polymer surface (Davarcioglu 2017; Kuswandi and Moradi 2019; Poonia 2019). Their performance was tested on Fior di Latte, soft cheese, soft-ripened cheese, and soft white cheese samples, as well as on milk powder or butter (Poonia 2019). Due to antimicrobial activity, zeolite-X and silver ions were investigated to create starch composite films by Elsherif et al. (2020). Starch films with zeolite-X and nanosilver were investigated as active packaging materials for pasteurized milk. Films with both zeolite and nanosilver demonstrated good antimicrobial properties and prolonged shelf life of milk up to 15 compared days to control. Silver nanoparticles are known for their antimicrobial activity. Their use in nanoscale provides relatively larger surface area compared to larger particles above 100 nm which in turn increases the antimicrobial activity at lower concentrations. Silver particles are also capable of inhibiting growth of thermoduric bacteria like *S. thermophilus* that can survive short-term heating (Basavegowda et al. 2020). Although they themselves can along with lactic acid bacteria inhibit the growth of some pathogenic bacteria through lactic acid production that is desired in fermented dairy products, but they can also lead to milk thickening (Braun et al. 2020). Singh et al. (2018) developed a PET packaging film with the addition of silver nanoparticles (AgNPs). The film was obtained by extruding virgin PET with recycled PET (waste-based in concentrations 5, 10, 15, and 20%) and then made into pouches to protect fresh white cheese at different temperatures (6, 25, and 40 °C) for up to 30 days. The antimicrobial activity of the PET/AgNPs packaging was tested against *S. aureus*, *E. coli,* and *C. tropicalis*. In this study, they also tested PET/AgNPs film with chitosan (Cs). The obtained results confirmed antimicrobial activity of active PET films. The PET/AgNPs/Cs film with the addition of 5% AgNPs demonstrated antimicrobial activity of fresh white cheese within 7 days at 40 °C.

Also bimetallic and trimetallic nanoparticles (NPs) have high antimicrobial and antioxidant properties. Intensely studied are silver and titanium dioxide (TiO_2) nanoparticles. Moreover, clay nanoparticles used in packaging materials have the ability to protect food from moisture, CO_2, and oxygen that can cause spoilage and decrease shelf life (Ligaj et al. 2020). Jin (2017) studied polylactide (PLA) films containing zero-valent iron nanoparticles antimicrobial properties. The obtained films were used as coatings on a polyolefin film and used as goat cream cheese wrappings. They were then tested against microorganisms *E. coli*, *B. subtilis*, *S, epidermis*, *R. rubra,* and *G. candidum*. The addition of 3% of zero-valent iron resulted in full microbial growth inhibition and lower concentrations showed little antimicrobial effect. The prepared wrapping protected goat cream cheese for 6 weeks (stored at chilled temperature). Moreover, the active packaging did not influence the natural microflora of the cheese. These findings are promising for active ripening and cottage cheese packaging which change their desired sensory properties during storage.

6.5.1.3 Essential Oil Coatings

The use of essential oils (EO) as antimicrobial agents in active packaging can prolong shelf life of dairy products. They are also generally recognized as safe (GRAS) and show wide spectrum of pathogen inhibition. EOs are of natural plant origin and are a mixture of volatile compounds like terpens, sesquiterpens, polyphenols, lactones, esters, alcohol, and others (Munekata et al. 2020). In cheese preservation, thymol and linalool essential oils have been known. Cheddar cheese stored at 15 °C over 21-days period in films containing thymol, carvacrol, and linalool effectively reduced the population of *S. aureus* (Jin 2017). Coatings with thyme and clove essential oils in addition of 1.5% demonstrated a decrease in *E. coli* O157:H7 strain in a semihard Turkish cheese (Kashar) during 60 days of chilled storage. Similar antimicrobial properties on Kashar were reported with the use of coatings with ginger (1.5%) EOs after 30 days of storage (Munekata et al. 2020). Another research proved antimicrobial properties of cinnamaldehyde in inhibiting fungi growth on white cheese samples. No fungi were present after 26 days of storage at chilled conditions (Irkin and Esmer 2015). Studies on the addition of EOs to dairy products have shown their antimicrobial properties. These substances could also be used in active packaging since they were successfully used in the products. Treating cheese with natural herbs is known in Italy (Casoperuto, Marzolino, Romano pepato, PiacentinuEnnese), Switzerland, France, Netherlands, Egypt, Syria, Morocco, and Turkey. For example, black cumin seed oil showed antimicrobial activity against pathogenic bacteria in soft cheese, whereas cayenne and green pepper demonstrated growth inhibition toward *S. aureus* in Egyptian Kareish cheese. Moreover, extracts of garlic, lemon grass, cinnamon, sage, salvia, rosemary, thyme, basil or oregano are able to inhibit the growth of *L. monocytogenes* in cheese (e.g., feta cheese, Iranian white cheese). Essential oils can be applied to packaging materials to extend their shelf life and to overcome the problem of defining precise quantity to be added to dairy products (Ritota and Manzi 2020).

6.5.1.4 Bacteriocins

Most of bacteriocins are produced by lactic acid bacteria (LAB); they are thermostable, hypoallergenic, and degrade in human gastrointestinal tract. They are low-molecular-weight peptides or proteins comprised of 30–60 amino acids (Jin 2017). One of bacteriocins is nisin, which is heat-stable, nontoxic, and exhibits a wide spectrum of antimicrobial activity, but also has a GRAS status. It is allowed for use in a range of dairy products like pasteurized cheese, mini red Babybel cheese, ricotta cheese, skimmed milk, soft cheese or BlatackeZlato cheese. Nisin can be immobilized on the surface of traditionally used polymers such as polyamide and polyethylene and in such have the ability to reduce LAB bacteria counts on, e.g., sliced cheese packed in MAP and stored at refrigerated conditions (Irkin and Esmer 2015). Nisin has shown to extend shelf life of raw and pasteurized milk stored at chilled conditions over a 4-day period and cheddar cheese over a 12-week period at 4 °C (Youssef et al. 2017).

6.5.2 Oxygen Scavengers

There are many dairy compounds that are susceptible to oxidative degradation such as lipids, vitamins (A, D, E, and C), carotenoids, chlorophyll, and anthocyanins. The process leads to quality deterioration and can take place at any point of the distribution chain. Usually in order to preserve dairy products from oxidation, preservatives are being used. However, due to health awareness and seeking for products with clean labels (as much natural as possible) by consumers, there is a growing necessity for development of different solutions. Antioxidant active packaging can be an alternative to traditionally used preservatives. These are packaging materials with incorporated antioxidants like oxygen scavengers (e.g., TiO_2, ferrous compounds metallic salts) in a form of sachets or labels (Bastarrachea et al. 2015; Kuswandi and Moradi 2019). Their action is based on release of antioxidant compound to food and subsequently scavenging undesired substances (Jafarizadeh-Malmiri et al. 2019). They can act either as migratory or nonmigratory antioxidants. Migratory antioxidant active coatings are designed to release the antioxidant in a controlled way during product's shelf life. Nonmigratory active coatings act as scavengers (e.g., oxygen, free radicals, and transition metals) and they do not require direct food contact as they can remove the undesired substances from the packaging headspace altering the conditions inside the packaging and prolonging shelf life. An advantage of nonmigratory active coating in comparison to migratory ones is that the active agents can be applied in lower concentrations which do not alter sensory perception of the product (Bastarrachea et al. 2015).

Active coatings can be an alternative to traditional cheese coatings in controlling the growth of microorganisms, loss of cheese weight, and drying of rind resulting in poor quality and economic losses (Youssef et al. 2017).

6.6 Intelligent Packaging for Dairy Products

Intelligent packaging (IP) solutions are developed to inform retailers and/or consumers of the quality and safety of food. They can monitor the conditions of the packed products and give information on temperature conditions in which the product was kept within the supply chain or the integrity of the packaging. Among IP, there are different indicators (time-temperature, gas/integrity, and freshness), data carriers (RFID, barcodes), and sensors (gas, temperature, biosensors, and nanosensors) (Davarcioglu 2017; Jafarizadeh-Malmiri et al. 2019; Tichoniuk et al. 2021). Intelligent packaging can be applied on the primary, secondary or even tertiary (transport) packaging in a form of labels or tags depending on the level at which the product and the conditions of its storage/transport in the supply chain are to be monitored.

Use of intelligent packaging can also help in reducing food waste as now much of the food wasted is due to overdue "use by" date printed on each food packaging. Retailers and consumers depend on that printed date and dispose of food when the date has expired. In some cases, such food can be still safe and of good quality, but in other it can be unconsumable even before the "use by" date, especially if there was abuse of storing or transport conditions within the supply chain, the integrity of a packaging was breached (Maskey et al. 2020).

6.6.1 Time-Temperature Indicators

Perishable food like dairy requires temperature control to minimize microbial growth and prolong shelf life. In retail, dairy products are usually stored at 0–4 °C and 4–10 °C at home refrigerators. These conditions, however, do not inhibit the growth of most fungi as they are psychrotrophic in general (Eshaghi et al. 2020). Temperature abuse can occur at any point in the dairy supply chain. That is why temperature monitoring as a quality and safety factors is crucial.

Time-temperature indicators (TTIs) are easy to read devices that are able to show full or partial temperature history of the packed product or it is thawing in case of frozen dairy products like ice-cream. In dairy products, TTIs can also be used in process control of pasteurization or high-temperature short-time pasteurization, sterilization or UHT treatments of milk to ensure that the desired temperature of the process was achieved. These indicators are based on several mechanisms such as mechanical, chemical, electrochemical, enzymatic or microbial irreversible reactions. Their response is visible usually in a color change or a color dye movement indicating temperature abuse above a set threshold (Tichoniuk et al. 2021).

TTIs are commercially available and well known in the US, Asia, and Australia. Examples with thermochromic ink are OnVu® or CoolVu® that can be used in time-temperature monitoring of dairy products (Drago et al. 2020). Their principle is based on an ink that is photosensitive. After activation with UV light, it is in a colored state that gradually returns to its initial colorless state at a temperature-dependent rate. It can be set at different length and temperature sensitivity by controlling the type of photochromic compound and UV light activation time (Taoukis 2010). Another example of an irreversible TTI label is Smart Dot® (Evigence, Israel) presented in Fig. 6.5.

These labels are activated upon placement at a packaging and their color changes gradually over time. This chemical reaction is irreversible and temperature-dependent, the higher the temperature the color changes faster (it does not change at all if kept frozen). Smart Dot® can be calibrated to match the shelf life of a given product in the range from hours to months.

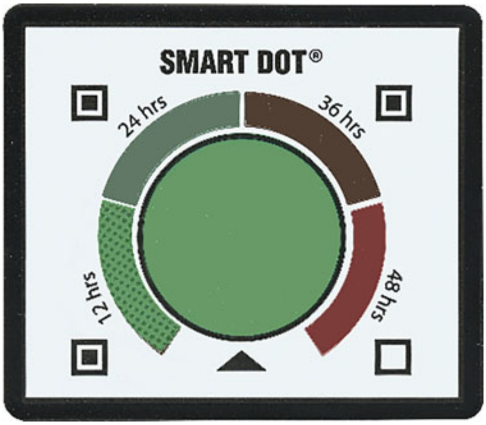

Fig. 6.5 Evigence Smart Dot® label (Source: Image provided by Evigence (2021))

6.6.2 Freshness Indicators

Freshness indicators can give information on the product's quality as they are designed to react with microbial growth metabolites like organic acids, glucose, volatile nitrogen compounds, carbon dioxide, ethanol, biogenic amines, and sulfuric compounds. They detect changes in pH or gas composition (Mirza Alizadeh et al. 2020).

Eshaghi et al. (2020) used a smart label containing beetroot color and multilayers of polystyrene (PS) for milk freshness analysis. They determined the changing label color by calculating label color number. At the beginning of the experiment, the label was dark red and the visible color change was observed in the fifth day of the study. The color started to fade slowly until it turned light brown after 7 days. During the experiment, milk pH, acidity and total bacterial count (TC) were investigated. The label responded to bacterial activity, and changing acidity in pasteurized milk during refrigeration storage. They found a positive correlation between the label color changes and TC, but also pH (Roohi et al. 2018).

Mimica (London, UK) offers a temperature-sensitive indicator for food freshness (Fig. 6.6) which monitors the temperature conditions of a product. The label feels flat in touch when the product is stored at desired temperature, but when there is a temperature abuse it feels bumpy when swiping finger over it. This bumpy feel indicates that the product is no longer good for consumption.

6.6.3 Integrity Indicators

Integrity indicators are used to support aseptic or modified atmosphere packaging (MAP) to maintain their functionality. They can be in a form of labels, tablets or printing on the inner side of the packaging. They can either detect an undesired gaseous component in the packaging (headspace) present as a result of leakage or as a volatile compound of the product spoilage. Integrity indicators change color giving

Fig. 6.6 Mimica freshness label (Source: Image provided by Mimica 2021)

a visible response easy to read in contact with the target gaseous compound. Unsealing of the packaging can lead to increase of oxygen concentration inside the packaging and as such can be detected with the use of an Ageless Eye oxygen indicator (Tichoniuk et al. 2021). Packed dairy products are susceptible to high oxygen levels which can contribute to product spoilage, undesired oxidation of lipids and micronutrients, growth of aerobic microbes, and also color, flavor, and odor changes. Maintaining low oxygen concentration in the packaging is crucial in MAP packaging. The above-mentioned Ageless Eye oxygen indicator is a colorimetric sensor in a form of a pink tablet that changes color to blue in the presence of oxygen ($\geq$ 0.5%) (Mirza Alizadeh et al. 2020).

6.6.4 Data Carriers

Data carriers are used in commerce and improve the purchasing process, inventory management, and traceability. According to Article 17 of the EU Regulation No 1935/2004, *the traceability of materials and articles shall be ensured at all stages in order to facilitate control, the recall of defective products, consumer information, and the attribution of responsibility*. Among traceability basic data are: producer's name and address, article number, and production date/identification of the product (Mania et al. 2018b).

6.6.4.1 Graphic Codes

This type of intelligent packaging systems includes well-known GS1 identifiers barcodes such as EAN-8, EAN-13 or code-128 (Fig. 6.7). The use of such graphic codes creates a standardized global data format that is readable in a product's life cycle (Vigneshwaran et al. 2019). They can facilitate product tracking from farm to fork.

Quick response (QR) codes (as presented in Fig. 6.8) are in some ways better or more advanced than traditional barcodes, as they can store mode data and can be readable by means of smartphones or computers (Tan and Ngan 2020). Those two

Barcode example

1 794623 037251

Fig. 6.7 An example of a Code-128 barcode (left) and EAN-13 code (right) (Source: generated at https://www.cognex.com/resources/interactive-tools/free-barcode-generator)

Fig. 6.8 Examples of QR codes (Source: own work)

dimensional (2D) codes have the ability to store more data than barcodes of up to 1.1 kilobytes (Mirza Alizadeh et al. 2020).

QR codes can encode more data thanks to different modes such as numeric, alphanumeric, binary, and kanji (Drago et al. 2020).

6.6.4.2 Radio Frequency Identification

Radio frequency identification (RFID) systems are an invisible reading mode in which data are decoded without human interaction (Tan and Ngan 2020). They are active tags that transfer data from a tag attached to a packaging to automatically track and trace it as well as identify it (Kuswandi 2016). RFID technology within the supply chain can improve inventory control, allow shelf life monitoring, and provide information on the temperature history of the product. RFID tags can also change the checkout method at the retail stores; because they do not require direct scanning of a readable barcode by a scanner. They simply need to be in the vicinity of checkout equipped with a RFID transducer. In the dairy sector, they are usually utilized to provide complete traceability of products (Mirza Alizadeh et al. 2020). Commercial applications of RFID solutions are brought by CAEN RFID (Viareggio, Italy) like an Easy2Log (A927Z), Easy2Log (RT0005) or qLog Temperature (RT0012) tags

Fig. 6.9 Examples of CAEN RFID tags: (**a**) Easy2Log - A927Z, (**b**) Easy2Log – RT0005, and (**c**) qLog Temperature (Source: Image provided by CAEN RFID (n.d.))

presented in Fig. 6.9. These tags can be applied in milk-based products. The A927Z is a low-cost, semipassive RAIN RFID logger tag with a rugged enclosure. It allows for temperature monitoring of perishable products. The tag can be used with standard RAIN RFID readers as it is compatible with EPCGlobal C1G2 and ISO 18000-63 standards. It can operate in the presence of strong vibrations and can store up to 8000 samples that can be preset in intervals from 8 s to 18 h. Alarms can be defined to control the temperature regime and when temperature is below or over a set threshold, user is informed.

The Easy2Log (RT0005) RAIN RFID tag is similar to the previously mentioned one. However, it can store up to 3958 samples and 16 temperature ranges with independent threshold alarms can be defined by user. It is also able to calculate the mean kinetic temperature thus enabling remaining shelf life configuration. The qLog Temperature tag is also applicable in milk-based products. It can store up to 4096 samples and their intervals can range from 5 s to 18 h. It has a rugged enclosure like the A927Z tag and can be used in air shipments. Moreover, it is equipped with an NFC interface which enables consumers to get information on the conditions of the product via smartphone (CAEN RFID n.d.).

6.6.4.3 Near-Field Communication

Near-field communication (NFC) is a technology that allows two NFC-enabled devices to communicate when held in close distance (ca. 4 cm). This technology evolved from radio frequency identification; here an NFC chip operates as one part of a wireless link. Once it is activated by another chip, small amounts of data between the two devices can be transferred. It does not require parring to connect the devices as it uses chips which are more power-efficient compared to other wireless types of communication. NFC smart packaging can be used to provide customers personalized experiences like with product information, promotional offers, how-to-guides, videos, and reordering reminders available with a simple tap of a smartphone. It can enhance brand loyalty as NFC tags are placed on each item, because they are small. This type of packaging has grown in popularity especially within the fast-moving consumer goods (FMCG). Yeo Valley Organic has introduced connected packaging across all products as part of the new “Put Nature First” brand platform. Consumers will be able to use their smartphones to scan the “Moo-R” QR codes which can be found on over 100 million products, linking to its “Yeokens” reward program, and bringing to life ongoing nature-led initiatives. Customers will have access to specific product information, brand content, and future promotions (AIPA 2020).

Maskey et al. (2020) designed a time-temperature history (TTH)-based wireless food label with an NFC antenna. The obtained label could be seamlessly integrated to the packaging. The label was designed by bridging a single Si-chip signal controller and transponder onto a roll-to-roll (R2R) gravure-printed antenna and thermistor. It was able to transfer logged temperature data to a smartphone using the ISO/IEC 15693 protocol. Such intelligent communication devices can inform retailers and/or consumers via smartphones of the product’s quality in real-time.

6.6.4.4 Blockchain Technology

Blockchain technology is a decentralized database that allows collecting and transferring information on the Internet network with peer-to-peer architecture. It is a distributed register of operations that are not handled by a single centralized server, but by computers connected together in a network. Information on these operations is stored here in batches (blocks) which are linked together by cryptography to form a blockchain. Blockchain is not governed by top-down authority and cannot be controlled by anyone. On the other hand, it is most often open source, which means that all its users have free access to it. More specifically, they can view the entire history of operations, but at the same time cannot edit any related data. What is more, every transaction that has been saved in the blockchain stays there forever. All these make blockchain an effective and secure way to store and transmit a variety of information.

This technology can be implemented to improve transparency and supply chain traceability “from farm to fork”. In other words, it can enable access to information like origins of raw materials, finished products, the different processes it underwent thus ensuring food safety and quality. However, there are not many dedicated applications and to lower costs companies try to take advantage of existing integrated enterprise information systems like ERP. The most implemented traceability solutions so far are RFID and barcodes which are used for example by Walmart, TESCO, METRO Cach&Carry (Tan and Ngan 2020).

6.6.5 Sensors

There is a growing consumer demand for ensuring the safety of food products. They can only rely on their sensory evaluation and “use by” date to determine the quality of a purchased food item. Smart packaging is therefore a kind of safety indicator and determines/monitors the quality of the product. Sensors are more sophisticated devices than indicators as they are made of a receptor and a transducer. They should be reversible in their action to constantly (in real-time) monitor changes within the packaging headspace or the product itself. Sensors are able to detect, locate or quantify target substance and describe its physical or chemical characteristics (Park et al. 2015; Pereda et al. 2018; Tichoniuk et al. 2021). They can detect gases released during spoiling of food, monitor pH, temperature or color of the packed food (Kuswandi 2016; Basavegowda et al. 2020). Berna (2010) mentioned SnO_2 and other metal oxide semiconductor sensors to detect adulteration, contamination or off-flavor in milk and dairy products. Such sensors used in electronic noses that detect volatile compounds are also capable of determining aging/ripening or cheese type, but also origin of milk or caseinates. Moreover, sensors can be an alternative to traditional methods such as chromatographic techniques coupled with for example, mass spectrometry (expensive, time- consuming, and labor intensive) (Campanella and Tomassetti 2019).

6.6.5.1 Nanosensors

This type of sensors can be used to detect microbial contaminants, toxins, foodborne pathogenic bacteria, and facilitate food testing. Nanosensors have the advantage over traditional methods that they can rapidly detect analytes like microbes, contaminants within minutes up to days. They can inform consumers and retailers of the product’s temperature, light or oxygen exposure history (Jafarizadeh-Malmiri et al. 2019; Basavegowda et al. 2020). In nanosensors, different particles in nanoscale can be used such as carbon tubes, nanoshells, dendrimers, quantum dots, nanorods, liposomes, and others. They are also able to detect allergens in dairy products (optical nanosensors). In addition, these sensors are capable of detecting gas content (oxygen, carbon dioxide) in the packaging headspace in a noninvasive and continuous manner, which is very important in MAP packaging systems to ensure packaging integrity (Kabariya and Ramani 2017).

6.6.5.2 Biosensors

First biosensors were designed in 1950s and since then they have been developed into more accurate and rapid solutions for monitoring food quality and safety. Their performance is based on their sensitivity, reproducibility, portability, high noise ratio, appropriate storage conditions, response time, and ease of use (Kabariya and Ramani 2017). Depending on the receptors used, there can be:

- Immunosensors
- DNA sensors

- Microbial sensors
- Enzymatic sensors (Chauhan et al. 2019)

They are comprised of protein, enzymes, oligonucleotide, cells or tissues that are used to generate a particular signal toward the objective analyte (Kabariya and Ramani 2017).

In dairy products like milk or cheese to detect pathogenic microorganism, a nanocomposite-associated smartphone-based immunosensor (pathogen—*S. enteritidis*) and UCNP-conjugated antibody biosensor (pathogens—*E. coli*, *S. aureus*) were studied. Moreover, to detect toxins in skimmed milk (botulinum neurotoxin A), a graphene oxide-based FRET biosensor and botulinum neurotoxin in milk and a graphene nanocomposite-based impedimetric immunosensor were investigated. There is also a commercially available sensor like Assurance® (Neogen Corp., USA) can detect enterohemorrhagic *E. coli* (EHEC) and *L. monocytogenes* in liquid milk (Chauhan et al. 2019).

Commercially available biosensor assay kit for determination of lactose levels in lactose-free or low-lactose dairy products is LactoSens®(DirectSens, Austria) shown in Fig. 6.10.

It consists of disposable test strips with an immobilized enzyme which oxidizes lactose in the sample and electrons are detected amperometrically by the detector as shown in Fig. 6.11 (Halbmayr-Jech et al. 2021).

Moreover, each strip has a QR label for sample tracking and lot-specific information. It is simple in its operation and requires only 1 mL of a liquid product sample or a homogenized solid sample and a portion (1 mL) of a LactoSens Buffer. Then the Reader is to be connected to a computer and a dedicated software changes the

Fig. 6.10 LactoSens® biosensor assay kit for lactose detection in dairy products (Source: Image provided by DirectSens (2021))

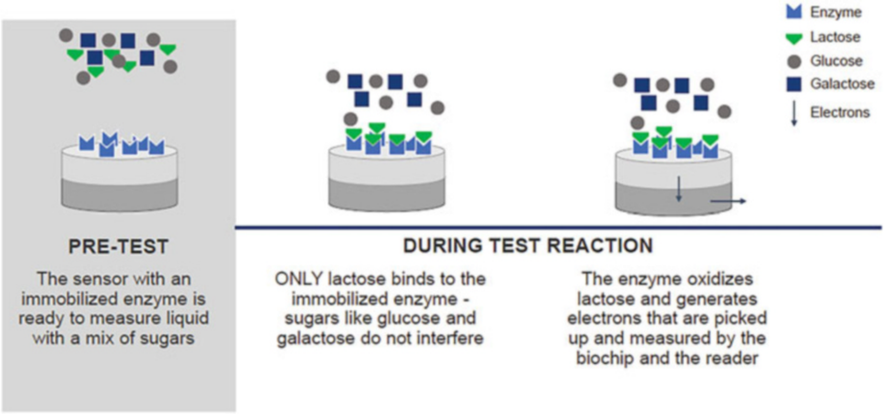

Fig. 6.11 LactoSens® mode of action (Source: Image provided by DirectSens (2021))

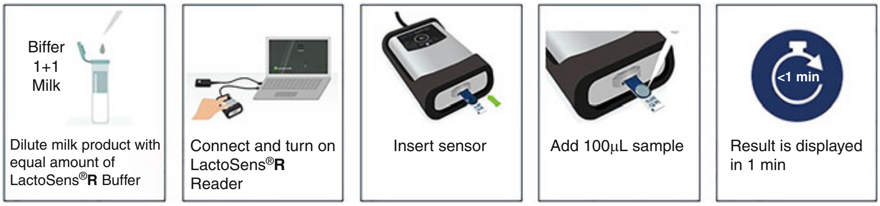

Fig. 6.12 LactoSens® operating procedure step-by-step (Source: Image provided by DirectSens (2021))

electrical signal into a lactose concentration (based on the specified calibration curve) (Fig. 6.12) (Halbmayr-Jech et al. 2021).

LactoSens® was validated according to AOAC Standard Method Performance Requirements (SMPR®) 2018.009 and the method was certified by NordVal in 2018. This is a rapid and selective method for determination of lactose in dairy products and products with dairy ingredients (Halbmayr-Jech et al. 2021).

6.7 Fraud in the Dairy Sector

Nowadays there can be observed two challenges in the dairy sector such as adulterations and counterfeit products and the second one being increasing the use of blockchain technology and traceability (Tan and Ngan 2020). Milk adulterations can take different forms such as addition of whey, melamine, starch, water, chlorine, formalin or mixing milk from different species. Moreover nondeclared substances can be added to milk and dairy products (e.g., urea, sodium bicarbonate, dicyandiamide) or mislabeling of geographical origin or as an organic food (Sharma et al. 2019; Hassoun et al. 2020).

Improved traceability and security (fraud control) of products, especially food products can be obtained through the use of global standard like GS1. The widely known and recognizable EAN-13 barcodes and the accompanying GTIN-13 numeric codes allow for better traceability of products in the supply chain and verification of their authenticity. The range of use covers 150 countries and about two million companies in the world. Each manufacturer has the rights to a specific GTIN-13 with which they can legally code their products (their brand). Unfortunately, with the growing popularity of e-commerce, the theft of these codes and impersonation of other companies under existing brands have increased. It is, however, possible to be picked up by GS1 and even taken to court. Therefore, from producers' perspective, better traceability allows for quicker response within the supply chain and products recall, but also fraud control enables maintaining the desired brand image, credibility in the eyes of consumers, and their safety. From consumers' point of view, those solutions/standards facilitate retail, especially in self-service stores and/or with self-service checkouts. These factors have become increasingly important in recent years (Mania et al. 2018b; Roohi et al. 2018). Traceability is crucial among other factors in dairy sector as it supports product quality and tacking in the entire life cycle of the product providing information even on rearing of milking cows. However, there was a necessity to develop a regional standard namely a Chinese Sensible Code that is adjusted to Chinese character environment (Li et al. 2015).

Also NFC tags provide product unique IDs that prevent counterfeiting and can support authentication of the product both by brand owner and consumer. Intelligent packaging is often utilized as tracking devices to ensure food security and avoid fake products (Davarcioglu 2017).

Development of tamper-evident packaging solutions is gaining speed. They are often additional packaging materials like special bottle liners or closures or changing color upon opening heat seals (Smirnova et al. 2020).

Among most counterfeited foods is milk, just after olive oil. This usually takes the form composition and quality falsification. Most common is diluting milk with water, milk whey, and addition of milk substitutes, preservatives, and N-containing substances. Milk fat is often replaced by cheaper plant analogs (Smirnova et al. 2020). In analysis of dairy products for adulterants like starch, urea, hydrogen peroxide, neutralizer, detergents, boric acid, melamine, mycotoxins or bacteria, different nanosensors can be used. Traditional methods are time-consuming, expensive, and require skilled personnel to conduct them. It is crucial to analyze the presence and amounts of those adulterants in dairy products and compare those concentrations with limits set by governmental food authorities around the world (Berna 2010; Kabariya and Ramani 2017). Examples of adulterants detected by means of nanosensors are presented in Table 6.3.

One of illegally added into dairy products substance is melamine which increases protein levels in the product. It is a small organic compound that is difficult to determine by a standard Kjeldahl method. In human bodies, melamine forms

Table 6.3 Adulterants and nanosensors used to detect them in dairy products

Dairy product adulterant	Nanosensor	Detection tool/technique
Melamine	Gold nanoparticle Water-soluble CdTe quantum dots Single-wall carbon nanotube	Colorimetric probe Standard colorimetric card Surface-enhanced Raman spectroscopy Fluorescence probe Electrochemical luminescence
Bacterial pathogens *Salmonella* *E. coli* O157:H7 *Staphylococcal enterotoxin B*	Carbon nanotubes Magnetic nanoparticles and TiO_2 nanocrystals Oligonucleotide-functionalized Au Gold nanoparticles	Electrochemical sensor Optical nanocrystal probes Piezoelectric biosensor Chemiluminescence
Toxins: Brevotoxins Aflatoxin Aflatoxin B1 Mycotoxin Ochratoxin A	Au NP-PAADs Functionalized-gold nanoparticles Silver core and gold shell Nanostructured zinc oxide Single-walled carbon nanotubes	Electrochemical immunosensor immunoelectrode immunodipstick assay indium-tin-oxide glass plate Fluorescent aptasensor

Source: Based on (Kabariya and Ramani 2017)

insoluble melamine-cyanurate crystals in their kidneys which can lead to kidney damage or death. There was a melamine scandal in 2008 in China as it was found in milk and lead to several infant deaths and thousands suffered from kidney failures (Yang et al. 2018; Sharma et al. 2019; Shellaiah and Sun 2019; Montgomery et al. 2020). Melamine in raw milk can be detected by dopamine-stabilized silver nanoparticles as a colorimetric reader. It is a one-step assay that is simple and rapid, but also of high sensitivity (Poonia 2019). Other nanomaterial-based melamine detectors like quantum dots, nanocrystals, nanorods, and nanotubes were reviewed by Shellaiah and Sun (2019).

As an example of product authentication, it is worth mentioning cases of counterfeiting Mozarella di Bufala Campana Protected Designation of Origin. Novel analytical methods have been proposed to differentiate milk and cheese product from Protected Designation Area from those produced outside of it (Hassoun et al. 2020).

Despite development of novel adulterations detection methods, the battle against counterfeiting of milk and dairy products is still a challenge. One of the reasons is that there are cases where it is difficult to define the type of fraud or detect it. Aiding the monitoring and assessment of contamination issues are various country regulations, governing bodies, and companies that run their own tests. There are also databases that gather and provide information on food safety like in the EU Rapid Alert System for Food and Feed (RASFF) of Fera'sHorizonScan or the EU Food Frau Network (FFN) (Montgomery et al. 2020).

6.8 Conclusions

Food waste and losses can occur at any point in the supply chain especially within perishable goods like dairy products. Millions of tons of food waste can be avoided through the use of proper packaging. They no longer simply protect the product, but also can prolong its shelf life and ensure customers of the product's quality, safety or integrity. The use of active packaging systems offers a variety of solutions supporting shelf life and safety. On the other hand, intelligent packaging improves product's traceability and provides much crucial information on the product's conditions or possible adulterations. Novel edible coatings allow for improved protection of dairy products, can also act as active compounds or nutrients carriers with controlled release. Moreover, they can be an alternative to plastic packaging and help minimize the use of petroleum-based packaging materials. Those novel technologies enable producers to adapt to the constantly changing requirements on the dairy market. In addition, they can support inventory and supply chain management, enhance traceability, as well as be environmentally friendly and contribute to reducing food waste.

Innovations on the food packaging market and in the area of dairy products are dictated by both the changing and constantly growing requirements of consumers, market participants, as well as economic and environmental aspects. Growing consumer awareness of the quality, safety, and health benefits of dairy products drives innovation in this market segment. In turn, to meet these requirements and to extend the shelf life of products, ensure their authenticity, and improve logistics processes, appropriate packaging is necessary. Packaging innovation goes along with product development and is part of the fourth industrial revolution (Industry 4.0). Novel packaging materials and solutions add value in the food supply chain. In addition, it can help to reduce food waste and economic losses.

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Functional Packaging Materials for Fishery Products Applications

7

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Abstract

Demand for fishery products is on the rise as it is regarded as health food due to their easily digestible protein with all the essential amino acids, essential fatty acids, vitamins and minerals in good proportion. However, they are also highly perishable due to their intrinsic properties apart from other external factors which affect their quality. Suitable processing and storage will enhance the eating quality of fish for an extended period. Processing methods adopted to preserve the quality of fishery products have to be appropriately supplemented with the selection of better packaging materials. Conventional packaging materials used for food packaging offer limited advantages. Apart from this, the petroleum-based packaging materials pose environmental problems if not properly managed. As a result, the demand for biodegradable packaging materials is increasing worldwide. Biomaterials from the aquatic origin are gaining increased attention in developing biodegradable packaging materials, especially with certain functionality. This chapter gives a brief note on the functional packaging materials like oxygen scavenging film, fish freshness indicating film, thermochromatic indicating film, antimicrobial film, antioxidant film, pathogen indicating film, off-odour scalping, flavour emitting films, etc.

Keywords

Functional packaging film · O_2-scavenging film · Antimicrobial film · Freshness indicating film · Thermochromatic film

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7.1 Introduction

The demand for very good quality fresh and minimally processed products is on the rise. Consumers do not want processing techniques adopted by the industry to affect both the nutritional and characteristic quality of the product. This has led to the development of minimal processing or novel food processing technologies which minimize the changes after processing and storage. Apart from processing, widespread awareness and advancements in hygienic handling, packaging and preservation have improved the quality of food products. The aim of consumer is to get best quality product for the price paid and at the same time food manufacturers strive to supply quality products with sustainable quality for an affordable price. Of the variety of options available for food, fish and fishery products have special importance. Historically, fish has long been an important part of human diets, and increasingly a major source of economic value. Globally, fish accounted 6.7% of all protein consumed by humans, as well as offering a rich source of omega-3 fatty acids, particularly EPA and DHA, vitamins, calcium, zinc and iron. There is a great demand for fish and shellfishes in international market due to its proven health benefits. Fish business not only provides foreign exchange it also helps in ensuring nutritious food, employment to millions of people, many of whom are below the poverty line. As per FAO (2018), the world fish production in 2016 has reached 171 million tonnes and 88% of this was used for direct human consumption. Of the total fish produced, aquaculture represented 47%. Global sale value of fisheries in 2016 was estimated at US$ 362 billion of which US$ 232 billion was the contribution from aquaculture production. The value of global fish exports in 2017 was US$ 152 billion, up from $8 billion in 1976 and 54% of this was originating from developing countries, indicating the contribution of seafood export to the building of nations. Nearly 57 million people are engaged in the primary fish production sector, a third of them in aquaculture. Of all the global merchandise trade, fishery products accounted for one per cent in terms of value, representing more than 9% of total agricultural exports. Export of fishery product is one of the major foreign exchange earners in developing countries which accounted to over US$ 80 billion in 2017, providing higher net trade revenues than meat, tobacco, rice and sugar combined. The per capita consumption during 2016 reached 20.3 kg and is expected to increase further. On an average, fish provides nearly 6.7% of all protein consumed by human beings. These indicate there is an ever-increasing demand for fish across the countries, which should be met by increasing the production.

Due to ever-increasing demand for fish, global requirement is increasing steadily. From the available data, it is observed that both fish production as well as fish consumption increased from 1975. Till 1990s, capture fisheries was the major contributor and later, the importance of aquaculture increased resulting in sizeable contribution to total production. As the years pass, the fish consumption level is also increasing. Per capita consumption was 9 kg in 1961 which increased to 17.2 kg in 2008 and further increased to 20.5 kg/year in 2018 (FAO 2020). Considering a stable consumption at 2008 level, the fish requirement estimated as nearly 140 and 152 million tonnes by 2025 and 2050, respectively. However, as the consumption is not stable and it is increasing steadily, the additional demand considering the rate of increase in consumption between 1975 and 2008 will be 164 and 232 million tonnes by 2025 and 2050, respectively. Meeting this huge demand is a herculin task, which creates huge pressure on both capture production as well as on aquaculture. As it is very important to increase the production of fish to meet the global demand, it is also equally important for its proper utilization without wasting by adopting responsible handling, advanced processing and packaging to reduce the post-harvest loss. It is estimated that, nearly 18–20% of global fish production is wasted as post-harvest loss resulting in huge loss of valuable nutrient-rich food commodity. This also affects the economy of the country negatively. For instance, in India alone, very huge economic loss is estimated annually, which is very huge loss to the economy as well as loss of nutritive food commodity. Proper handling of food including fish from its primary production centres and processing them into suitable forms, packaging and storage at desirable temperature will help in reducing the post-harvest losses. Proper handling for fishery products includes segregation of catch based on species and size. Evisceration of large size fishes and icing of fishes with appropriate fish to ice ratio is the first step immediately after catching fish for maintaining better quality. Avoiding more than 3 layers of stacking of fish and ice to avoid damage to fishes in the bottom layer is another good handling practice on board the fishing vessel. Upon arrival at landing centres, care should be taken to unload as early as possible. They should be placed on the raised platform/surface/floor which can be easily cleaned and chlorinated after the auction is over. Processing factories should receive only good quality fish which have maintained the minimum temperature of <4 °C. Once it is processed in suitable form viz., chilling, refrigerated, freezing, curing and drying, thermal processing, smoking, freeze-drying or developing value-added products, they have to be properly packed and stored at the proper temperature. Packaging material should be chosen wisely so that it will complement to the processed food product to extend the eating quality maintaining all the desirable quality.

Food packaging in simple words is wrapping or covering or placing in sealable materials to give protection from its external environment to preserve the quality for an extended duration or till it is utilized by consumers. Although all the activities including processing with advanced techniques are practised with utmost care and if the packaging techniques and packaging materials are not selected suitably it may not protect the food as it is expected. Hence, it assumes great importance to offer the required characteristics to the food till the end of shelf life. Proper packaging not only protects the food from chemical changes during storage, microbial contamination arising from its external environment but also prevents physical damage from the wear and tear during handling, transportation and storage. If the products are not packed properly, the packaging process can become a source of contamination. The main purpose of packaging is to provide protection from biological hazards (pathogens and spoilage organisms), pests, physical damage (shock or vibrations), should act as barrier to external gases, moisture and light, and should provide protection during storage, handing and distribution and transportation. Packaging also provides information about the product contained with ingredients, nutritional information, allergens if any, manufacturer details and also manufactured date. The concept of packaging is also fast changing as the modern packaging is also intended to provide security against tampering, counterfeit by providing authentic seals and helps in tracking and tracing the product.

Traditionally, food packaging is aimed for protection, communication, convenience and containment (Paine 1991; Robertson 2006). Packaging material intended to be used for food package should be able to withstand the internal pressure as in the case of vacuum packaging and modified atmosphere packaging, should be able to withstand the processing conditions like high temperature and pressure as in the case of thermal processing, should be able to withstand storage conditions like normal room temperature, chilled or refrigerated temperature, frozen temperature or elevated temperature as desired to maintain its quality and shelf life, should withstand process conditions and machinability. External factors which are considered for protecting food include but not limited to conditions like heat, light, presence or absence of moisture, pressure, gases, microbial contamination, etc. Convenience and time-saving attributes and different attractive shape and size of package to contain the products are other advantages offered by the packaging materials (Yam et al. 2005; Marsh and Bugusu 2007). The inertness of the packaging material was the key safety objective for traditional packaging materials.

7.2 Overview of Food Packaging Industry

Packaging industry is growing rapidly due to its ever-increasing importance. Globally packaging industry accounts to 700 billion US$ excluding turn-out for machineries. The United States of America is the major market for packaging materials accounting nearly 24% of the global market. European Union is the second largest market and Germany, France, Italy and UK dominate packaging industry in Europe. Among the different packaging materials, paper and board lead the sector with 36% of the world market followed by petroleum-based packaging materials. World food packaging market size is to the tune of over 300 billion US$ in 2019 and is expected to increase to more than 460 billion US$ by 2027 (https://www.fortunebusinessinsights.com/industry-reports/food-packaging-market-101941).
Glass, metal, paper & paperboard, wood and plastic packaging materials are widely used for a variety of food sectors like fruits and vegetables, meat, poultry and seafood, dairy products, bakery and confectionery, sauces, dressings, condiments, etc. Changing lifestyle, convenience, increasing purchase power, increased percentage of working women and crave for spending more valuable time with the family are the factors influencing the growth of packaged food and beverages apart from extended and stable shelf-life with improved safety and quality. Rising consumer awareness and demand for processed food is another factor influencing the growth. Multinational giants taking rapid strides in the food and beverages industry is another important factor influencing the growth of food packaging industry. As a result, the per capita consumption of packaging food is worth US$ 400, 260, 90, 46 and 9 for the USA, Europe, Latin America, Asia and India, respectively. Being one

of the fastest-growing industries, it is expected that the food packaging industry will grow to new heights.

7.3 Selection of Packaging Material

Appropriate packaging material should be chosen based on the composition of the food. The use of proper packaging will ensure the safety and durability of the product during its entire shelf life. Important aspects to be considered while selecting packaging materials are its moisture content, sensitiveness to oxygen, acidic or alkaline, alcohol content and fat content. A container that is appropriate for one type of food may not be suitable for another. It is very important to choose the proper packaging for the food intended to pack. The packaging materials/packages used in fish industry are both modern as well as traditional types, ranging from bamboo baskets, jute bags, leaf mats to corrugated fibre-board boxes, duplex board cartons, metal containers of aluminium and tinplate, plastic films and their laminates, thermoformed trays, polypropylene/high-density polythene crates, expanded polystyrene insulated boxes, glass bottles, etc. Each packaging material has its own merits and demerits. Paper & paperboards are very common packaging materials used for wide applications. These are made using pulp extracted from wood and other non-wood sources like straw, bamboos, etc. As wood pulp is very easily accessible, and commonly available its use is on the rise. Due to its natural and low price, it is one of the preferred packaging materials. They are suitable for small-scale, large-scale, retail and bulk packaging. All kinds of foods can be packed using paper and paperboard after slight modifications. They can be used as bags, pouches, wrapping, boxes, cartons, tetra packs, folding cartons, etc. The presence of cellulose fibres provides them good rigidity and high shock resistance. They are also light in weight, cheap and are widely available. However, they need to be laminated for packing foods with moisture content. They also need external protection during transportation to protect from damage. Apart from this, they have to be stored in proper facility to prevent damage by rodents and insects. Another important aspect to be considered is the selection of safe wood for the manufacturing of paper and paperboard which comes in contact with food directly. It is common practice to use chemical preservatives to protect wood. Care should be taken to select the preservative free wood. Due to its sustainability nature, the paperboard will be the most prevalent and attractive packaging material in the food industry in future due to increased investments leading to innovations in packaging design and digital printing.

Glass is commonly used as packaging material for a variety of foods due to its inertness. Glass containers are manufactured by heating the mixtures like silica (sand), calcium carbonate in the presence of sodium carbonate (melting agent) and alumina (hardner) at very high temperatures to melt the mixture, cast them into the mould to get suitable shape and size and finally cooling them (Keleş 1998; Marsh and Bugusu 2007). Surface coating and oiling is done during the production process to prevent the abrasion of the glass surface (Aday 2014). Normally soda-lime glass is used in the packaging industry for producing transparent, transluscent or coloured glasses. Also, to mask the colour emerging from minute quantity of impurities like iron and sulphur compounds especially during the manufacturing of colourless glass, nickel and cobalt are added (Keleş 1998). Glass is one of the highly preferred materials for food packaging due to its inertness, durable, transparent, touch as it withstands high temperature and pressure, impermeable to gas, odour, liquids and water vapour (MEB 2011). It has a very smooth and shiny surface, it will neither corrode nor degrade or erode over time. However, they are not devoid of drawbacks. Major drawback is its heaviness and very fragile leading to break. It requires extra care while transporting and distribution and hence are more costly than petroleum-based packaging materials. Being transparent, it allows light to pass through the glass resulting in light-induced oxidation and discolouration.

Metal is another important material for packaging applications. Unlike glass, metals have free and mobile electrons that absorb light energy. That is why they cannot be transparent and translucent as in the case of glass. There is a long history of packing food products in metal containers. Mainly tin plate or aluminium or stainless steel coated with the food-grade lacquer material is commonly used. Among these, tin-plate containers were very commonly used for many food applications. Tin plate was used to make containers for food over 120 years. Tin-plate containers are very attractive and have an appealing golden colour. Tin can is made up of 98% steel and 2% tin coated on both the sides of container differentially. The surface coming in contact with the food material is coated thicker layer of tin. Normally low carbon steel is used in the manufacturing of this type of can. They are light in weight, rigid, strong, corrosion-resistant and easy to handle. They are comparatively easy to fabricate and offer more shelf life to food products compared to other metal containers. The major drawback of this container is its limitation for packing acidic products. In the earlier days, 3-piece cans were used soldering with a lead:tin ratio of 98:2 percentage. Some lead from this solder may migrate to food depending on the type of product packed and on the amount of solder exposed. Apart from this, lead contamination may also originate as impurity from the tin coating. Due to its proven ill effects, regulatory agencies have stipulated a maximum level of 2 ppm for lead in canned food products. Apart from this, tin may also permeate into the food and higher levels of tin will implicate in the gastro-intestinal disturbance. A level of up to 250 ppm is generally permitted by regulatory authorities in canned foods. Invention of 2-piece, solder-free cans reduced the problem of lead in canned foods. Canned shrimp products from India were very well appreciated from many importing countries and this industry was flourishing until 1980s. Later on the canned seafood industry collapsed as it could not compete with the neighbouring countries in terms of its pricing. As India does not have tin resources, it has to import tin-plate for manufacturing cans and hence it became costlier. This has resulted in search for other alternative metal cans. Aluminium is one such metal used as an alternative to tin-plate cans. In India and also in many parts of the world, aluminium is very abundantly available and is light in weight. It is recognized as generally regarded as safe (GRAS) material by the US FDA. The use of 100% aluminium for manufacturing cans or containers results in weak material. To overcome this, small amount of magnesium, manganese, iron, zinc, copper and silicon is added while manufacturing. Aluminium-based containers can be used as cans for meat and fishes, beverages and as bottle tops or closures. Aluminium is easy to fabricate and one cannot make out the corrosion due to its colourless character. Metallic taste is not imparted when aluminium containers are used as compared to tin cans. Requirement of very high energy for the production, tendency to bleach with some pigmented foods and impossibility of soldering are the drawbacks of this container. Apart from this, aluminium is implicated in Alzheimer's disease up on chronic exposure from water and food. World Health Organization (WHO) has stipulated the limit of 1 mg kg^{-1} body weight per day. Tin-free steel is another metal container used for a wide range of food products like fruits, vegetables, meat and seafood. TFS cans are made by electrolytic coating of a thin layer of chromium and chromium oxide on the steel base material. The presence of chromium helps in preventing rust formation and corrosion. It can withstand very high internal pressure and is suitable for attractive printing. The major problem with this container is it cannot be recycled or reused and is not suitable for soldering or welding.

Petroleum-based plastic packaging material is another widespread material used for many applications including food packing. Plastic is the material that is obtained when the bonds between carbon and hydrogen, oxygen, nitrogen and other organic or inorganic elements are broken from their simple structured molecule, known as 'monomer' and formed into the long and chained structure, known as 'polymers' (Durusoy and Karababa 2011; MEB 2011). With the help of polymer science and engineering, many variety of plastics with varying characteristics can be manufactured so that almost all the food products with varying processing, storage and transportation conditions can be packed with plastic materials. Their lightweight, transparent/translucent with low or high gas and moisture barrier properties, requiring less storage space and easy to use, seal, open and dispose makes one of the most preferred packaging materials for food products (Kızılırmak 1997). They can be made either as thin films or as rigid containers depending on the requirements. Different packaging materials with their code and applications are given in Table 7.1. Codes from 1 to 7 are given for easy identification during its recycling. Different types of packaging material either single-layered or multi-layered packaging materials have to be selected appropriately depending on the category of food products which is given in Table 7.2. Among the different packaging materials, not all the materials are suitable for direct food contact application. The use of plastics and plastic-based materials are increasing across the food industry including fisheries.

Table 7.1 Different packaging materials and their applications

Code	Name	Applications
1 PET	Polyethylene terephthalate	Water and soft drink bottles
2 HDPE	High-density polyethylene	Bottles for milk, juice, water, yoghurt, cosmetics, shampoo, dish and laundry detergent, bleach bottles, ice boxes
3 V	Polyvinyl chloride (PVC)	Bottles packaging sheet, pipes and fittings from hard PVC, wire and cable insulation, film and sheet, floor coverings synthetic leather products, coatings, blood bags, medical tubing etc. from soft PVC
4 LDPE	Low-density polyethylene	Frozen food packaging and for squeezable bottles
5 PP	Polypropylene	Retortable pouches
6 PS	Polystyrene	Lids, cups, bottles and trays, food service applications, meat trays, egg cartons
7 OTHER	Other	Multi-layer combination, plastic baby bottles, clear plastic "sippy" cups, sports water bottles, metal food can liners, some juice and ketchup containers, compact discs, cell phones, computers

During the manufacturing of plastic packaging materials, along with basic polymer materials, other non-polymeric compounds are added either inherent or deliberately to achieve desired properties. These are categorized into three different classes viz., polymerization residues (residual monomers, catalyst remnants, polymerization

Table 7.2 Selection of packaging materials depending on the processing method for different food category

Food categories	Packaging material
Fresh chilled	HDPE, PP, HM-HDPE
Fresh frozen	Laminates or co-extruded pouches, LDPE, BOPP
Dried	HDPE woven gusseted sack, laminates
MAP	Nylon/suryln laminates, PVC moulded trays laminated with polyethylene, polyester/LDPE film, EVOH
Thermal processed	Metal cans, retort pouches, HIPP trays
Surimi	LDPE/LLDPE/HMHDPE with waxed duplex carton & 5/7 ply CFB
Sausage	PVDC or natural casings
Breaded & battered products	Thermoformed trays of PVC, HIPP & HDPE
Pickles	Glass bottles or PEST/LDPE-HDPE co-extruded film

Table 7.3 Limits of monomer and heavy metals in plastics

Country	Monomer	Heavy metals
BIS-India	VCM in PVC-1 ppm; in food migration-10 ppb, styrene in polystyrene-2000 ppm	Lead 1 ppm and others 0.01 ppm in PVC
EEC-Europe	VCM in PVC-1 ppm	Nil
EPF-UK	VCM in PVC-1 ppm, styrene in PS-5000 ppm	Nil
Japan	VCM in PVC-1 ppm, volatile component in polystyrene-5000 ppm Vinylidine chloride in PVDC-6 ppm, Caprolactum in Nylon-15 ppm	1. Lead, Cadmium & Barium 100 ppm each in PVDC 2. 0.05 ppm antimony & 0.1 ppm germanium in PET
FDA-USA	VCM not specified styrene in PS-10000 ppm, acrylonitrile in ABS plastics-11 ppm	Nil

VCM Vinylchloride Monomer, *PVC* Polyvinylchloride, *PVDC* Polyvinylidenechloride

solvent, etc.); processing aids (plasticizers, stabilizers, antioxidants, slip agents, lubricants, antistatic agents, etc.) and end-use additives (antioxidants, brighteners, blowing agents, mould release agents, colourants, UV stabilizers, etc.). Among these, the polymerization residues compounds are unavoidable whereas processing aids and end-use additives are deliberately added to the polymer either during manufacture or subsequently to achieve the desired end properties of the finished plastic material. If we are not adding these additives, desirable properties of the plastic packaging materials will not be noticed in the end product. Polymers by their nature like very high molecular weight and low solubility in both aqueous and fatty systems may make them inert. The other additives, which are non-polymeric in nature, are lower molecular weight which may leach out from these plastic packaging materials and dissolve in the food system. These may pose threat to human health due to their risk factor and the awareness in this matter has led the national and international regulatory authorities in the formation of guidelines for the proper use of plastics for food packaging application. Such guidelines are necessary to restrict

Table 7.4 Limits of heavy metals in colours used in plastic manufacture

Heavy metals	Limit (ppm)
Lead	0.01
Arsenic	0.005
Mercury	0.005
Cadmium	0.20
Selenium	0.20
Barium	0.01

the indiscriminate use or abuse of plastics in food packaging. The residual monomer content and heavy metal content in different plastics specified by different countries and limits of heavy metals in colours used are presented in Tables 7.3 and 7.4 respectively. The other regulations on food packaging materials comprise of regulations for adjuvants (antioxidants, colourants, plasticizers, etc.) used in food packaging materials. Only permitted materials within their allowable limits can be used in the manufacturing of plastic packaging material.

Packaging protects, but it is also a potential source of risk. Plastics, paper, cardboard, and other packaging materials that come into contact with the food can react with it and affect its safety. The plastic packaging material may contain impurities such as leftover monomer residues, additives, stabilizers, odorous adjuvants, colorants and antioxidants. At different stages of converting, preparing and storing, chemical substances may migrate to the food. If the packaging is made from wrong materials which include printing substrates like, inks, varnishes and all the auxiliaries used in the printing process, it may pose a risk to the packed product, thus to human health. In paper, the group of potential contaminants include 1,2-benzisothiazoline-3-one (BIT); 2-(thiocyanomethylthio) benzothiazole (TCMTBT); 2,4,5,6-tetrachloro-isophthalonitrile (TPN); 2,4,6-trichlorophenol (TCP); pentachlorophenol (PCP); 4,4′-bis (dimethylamino)-benzophenone; 4,4′-bis (diethylamino)benzophenone; 4-(dimethylamino) benzophenone (DMAB) and bisphenol A (BPA), which in chlorinated form (BPAs) may be found in effluent from wastepaper processing plants. Sometimes even slimicides and fungicides used in both virgin and recycled paper may pose risk to consumers. Pentachlorophenol is used for wood conservation, therefore if the conserved wood or slimicides containing this substance are used in paper production there is a risk of contamination of packed food. Leaching of all these chemicals from packaging material into food affects the quality of food and increases the risk to consumer. Hence the materials coming in contact with food product need to comply with strict regulations in many countries. It is the manufacturer's sole responsibility to deliver safe packaging materials which comply with all legal requirements. Due to this as well as due to the impact of these packaging materials on the environment and biota after disposal, there is an increased priority worldwide for the development of biodegradable packaging material which will not impact any health risk to consumers.

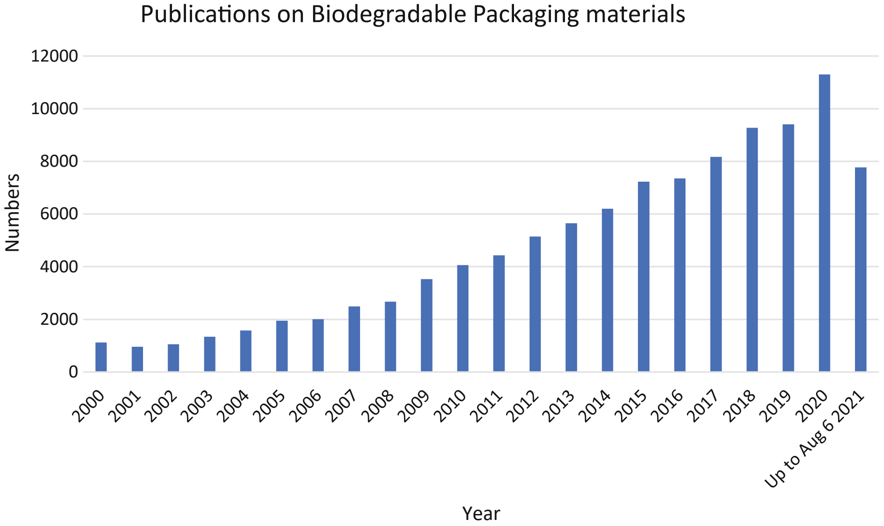

Fig. 7.1 Number of publications on Biodegradable packaging materials over the period 2000 to Aug 2021

7.4 Biodegradable Packaging Materials

Biodegradable packaging materials are the materials derived from natural biological materials. This can be either plant- or animal-based packaging materials. The research interest on the development of biodegradable packaging material is on the rise constantly from 2000 onwards as indicated from the publications (Fig. 7.1). In 2000, the publications were only 1120 which have crossed 11,000 in 2020. The growing interest is basically due to its eco-friendly, sustainable nature and will not create any health or environmental related issues. These biodegradable packaging materials can be either protein-based or carbohydrate-based materials in addition to a plasticizer. They can be in the form of gels, film, bag and box. As the biodegradable packaging materials are made using eco-friendly materials, their recycle will be easier. They require less energy to produce and are non-toxic in nature. Their carbon emission will be very less. Long-term and increased dependence on the biodegradable packaging material may result in requirement of more plant- or animal-based matter for their production. If any additives or petroleum-based polymers are mixed in compounded packaging materials, they require special facility for composting. The physical barrier properties are very poor compared to petroleum-based materials and not all the biodegradable packaging materials are sealable. Bioactive ingredients derived from aquatic sources which can be used for biodegradable packaging material production are fish and shellfish proteins, protein from Surimi waste, blanched and cooked water protein extract from heat processing, protein extract from clam shuck water, chitosan extracted from shrimp, crab, lobster and squid pen, collagen and gelatin from fish scale and skin, squid and cephalopod skin and a variety of seaweeds. Although biodegradable packaging materials have various advantages, functionalizing these packaging materials will increase their applications and enhance the quality of food products.

7.5 Smart Functional Packaging Materials

Globalization and dynamism in the exchange of food products, along with reduced time for selection/cooking with fresh ingredients, and the growing interest in health safety and environment are the main challenges which trigger the development of new improved packaging concepts. Traditionally, the functions of the packages include protection, containment, communication with the user, ergonomics and marketing. However, in recent years additional functions are incorporated into the packaging materials to meet the growing global demand on the safety of food products. One of the main objectives of food law is the safety of the food products. Controlling the quality and assuring the safety of the product at all the stages of food supply is very much essential to enhance the market reach for a product. This can be achieved by using active and intelligent packaging technology, which is also known as smart packaging. Active packaging involves altering the surrounding environment of food suitably with favourable gases, antimicrobial and antioxidant agents, flavour bearing compounds, etc. whereas intelligent packaging monitors interaction between the food, the packaging, and the environment and provides information like the conditions of the package, freshness, leakage and presence of pathogen and informs to the manufacturer and consumer. Thus, the smart packaging provides a specific functionality beyond function physical barrier between the food product and the surrounding environment. Knowing information about the product quality, the packaging or the environment establishes a bond of responsibility throughout the food supply chain (storage, transport, distribution and sale). The global market for active and intelligent packaging will double between 2011 and 2021, growing at an annual rate of 8% until 2016, reaching US$ 17,230 million, and later at an annual rate of 7, 7%, reaching US$ 24,650 million in 2021. Among the smart packaging technologies, the development of intelligent packaging material which can detect the presence of pathogen assumes great importance as it can assure the safe and wholesome food to consumers without any microbial pathogen contamination. The technology of developing smart pathogen indicating film can be used in all the food products to monitor the quality and safety of food from the producers to the consumers. The technology provides an on-line quality control and safety for the consumers beyond the existing conventional technologies which are helpful for the authorities and food producers as well.

7.6 Active Packaging

Active packaging is an advanced concept that can be defined as '*a type of packaging that changes the condition of the packaging and maintains these conditions throughout the storage period to extend shelf-life or to improve safety or sensory properties while maintaining the quality of packaged food*' (Vermeiren et al. 1999). Unlike other conventional packaging methods wherein packaging material or packaging system will not alter and remain passive in nature apart from their inertness. Any gases formed or introduced in the packaging atmosphere may escape or may enter from external atmosphere depending on the permeability of the packaging material resulting in alteration of the package atmosphere which affects the quality and shelf life of the product. In the case of active packaging, the packaging provides extra protection by interacting with the package atmosphere and modify the conditions of the package suitably to help the retention of the quality. This can be achieved either by removing undesirable constituents like oxygen, CO_2, off-odour, ethylene or by releasing suitable constituents like nitrogen, carbon dioxide, antimicrobials, antioxidants, ethanol, pesticide, etc., depending on the food products. Major active packaging techniques are concerned with substances that absorb oxygen, ethylene, moisture, carbon dioxide, flavours/odours and those which release carbon dioxide, antimicrobial agents, antioxidants and flavours. The most important active packaging concepts for fishery products include O_2 scavenging, CO_2 emitters, moisture regulators, antimicrobial packaging concepts, antioxidant release and release or absorption of flavours and odours.

7.6.1 O_2- Scavenger

Oxygen is a lifeline for all the animals when they are in living condition but becomes detrimental as soon as life is lost leading to spoilage and decay. Many food products including fish are highly sensitive to the presence of oxygen as it leads to the growth of aerobic microorganisms and oxidation which causes undesirable colour changes (e.g. discolouration of pigments such as myoglobin, carotenoids), off-odours and flavours (e.g. rancidity as a result of lipid oxidation) and leads to loss of nutrients (e.g. oxidation of vitamin E, β-carotene, ascorbic acid) which adversely affects the quality. Hence control of oxygen assumes its importance to control the spoilage and enhance the shelf life. This can be achieved by packing in high barrier films like EVOH, polyester-laminated with aluminium foil or laminated packaging materials. Further advanced packaging technologies like vacuum packaging and modified atmosphere packaging may be adopted. However, these techniques may not remove oxygen completely and there is no control on the permeation of oxygen through packaging materials. In such cases, the use of oxygen scavenger is highly suitable and very effective in reducing the oxygen level to very low level like less than 0.05% within short time. O_2 scavengers were first commercialized in the late 1970s by Japan's Mitsubishi Gas Chemical Company (Ageless®). O_2 scavenging concepts are mainly based on iron powder oxidation, ascorbic acid oxidation, photosensitive dye oxidation, enzymatic oxidation (e.g. glucose oxidase and alcohol oxidase), unsaturated fatty acids (e.g. oleic or linolenic acid), rice extract or immobilized yeast on a solid substrate. These oxygen scavengers are useful in preventing discolouration of fresh and cured fish, rancidity problems, mould spoilage of intermediate and high moisture products or oxidative flavour changes. Apart from fish, they find its applications in most of the dried food items like grains, snacks, bakery items, fish and meat, dry fruits, ready meal, etc.

O_2-scavenging film is developed either incorporating any oxygen scavenging systems mentioned above or by using the principle of photosensitive dye oxidation. This involves sealing of a small coil of an ethyl cellulose film containing a dissolved photosensitive dye and a singlet O_2-acceptor in the headspace of a transparent package. Due to illumination of the film with the light of the appropriate wavelength, excited dye molecules sensitize O_2^- molecules, which have diffused into the polymer, to the singlet state. These singlet O_2^- molecules react with acceptor molecules and are consumed (Rooney 1985):

$$\text{Photon} + \text{dye} \rightarrow \text{Dye}*$$

$$\text{Dye} * + O_2 \rightarrow \text{Dye} + O_2*$$

$$O_2 * + \text{Acceptor} \rightarrow \text{Acceptor oxide}$$

$$O_2* \rightarrow O_2$$

O_2 acceptors can be tetraphenyl porphine (TPP), dimethyl anthracine (DMA), dioctyl thallate (DOT), etc. This can be used for both wet and dry fish products as it does not require any moisture for its activation. Most O_2 scavengers in commercial use today are iron-based systems and only limited reports are available on film based O_2 scavenger.

7.6.2 Antimicrobial Packaging

Antimicrobial packaging is the second commonly used active packaging system after oxygen scavenger. The concept of antimicrobial packaging was developed due to increased awareness on the antimicrobial agents used directly by the food manufacturer to retain the quality of food. As microbial spoilage is the major cause for food deterioration, various chemicals were used for treating food to reduce both food spoilage and pathogenic microorganisms. The classes of these antimicrobial agents include but not limited to alcohol (ethanol), ammonium compound (quaternary ammonium salts), antibiotics (natamycin), antimicrobial peptides (leucocin, sakacin, enterocin), antioxidant phenolic compounds (butylatedhydroxyanisole (BHA), butylatedhydroxytoluene (BHT), tertiary butylhydroquinone (TBHQ), grape seed extract, pomegranate peel and seed extract), bacteriocin (bavaricin, lacticin, nisin, pediocin), chelators (citric acid, EDTA, lactoferrin, polyphosphate), enzymes (chitinase, ethanol oxidase, glucose oxidase, glucosidase, lysozyme, lactoperoxidase, hydrolase), fatty acids (lauric acid, palmitoleic acid), fungicide (benomyl, imazalil, sulphur dioxide), metals (copper, silver), natural phenols (catechin, hydroquinones), organic acid (acetic acid, benzoic acid, citric acid, lactic acid, propionic acid, sorbic acid, tartaric acid), organic acid salt (potassium sorbate, sodium benzoate, acetic acid, propionic acid, benzoic acid, sorbic acid, calcium sorbate, benzoic anhydride, propionic acid, propyl paraben), paraben (ethyl, methyl and propyl paraben), plant based volatile compounds (allylisothiocyanate, cinnamaldehyde, eugenol, terpineol, thymol), polysaccharide (chitosan, carrageenan), etc. Recent advancements in the nanotechnology research have expanded the list of antimicrobial compounds with silver nanoparticle as one of the highly potential antimicrobial agents. The principle action of antimicrobial films is based on the release of antimicrobial entities into the food which extends the lag phase and reduces the growth phase of microorganisms in order to prolong shelf life and to maintain product quality and safety. To confer antimicrobial activity, antimicrobial agents may be coated, incorporated, immobilized or surface modified onto package materials. However, there is a growing concern both by consumers and by the regulatory agencies on the very high levels of these antimicrobial compounds in the food products if they are used directly to treat with these antimicrobial agents. The residual levels will be very high leading to increased concerns which can be overcome with the adoption of active antimicrobial packaging techniques. The antimicrobial compound embedded into the polymer acts by two different kinds of mechanisms. In the first method, the preservative is covalently immobilized into the polymer matrix and acts directly from the film when the food is brought in contact with the active material. Regarding the latter, the preservative is embedded into the matrix in the dry state. When the active material is brought in contact with a moist food or a liquid-like food, the preservative is released from the material and acts directly. In both cases the aim of the system is to extend the shelf life of the packaged foodstuff, inhibiting the microbial growth and preserving its properties. The classes of antimicrobials listed range from acid anhydride, alcohol, bacteriocins, chelators, enzymes, organic acids and polysaccharides. Several compounds tested for antimicrobial activity in food packaging including organic acids such as potassium sorbate, sorbic acid, propionate and benzoate or their respective acid anhydrides, bacteriocins, e.g. nisin and pediocin, enzymes such as lysozyme, metals, fungicides such as benomyl and imazalil, Ag- zeolite. Antimicrobial agents are selected based on their ability to withstand the processing or extrusion condition of the packaging material and its compatibility. Ethanol is another commonly used antimicrobial agent for surface immobilization with the polymer films. At a concentration of 60–70%, v/v, it exerts its effectiveness. Even at relatively low concentrations (4–12%), ethanol has proved effective in controlling growth of several moulds and bacteria (De Kruijf et al. 2002). Spraying ethanol onto fresh or dry fish prior to packaging can be adopted, but another option is to use sachets generating ethanol vapour. This contains food-grade ethanol embedded or absorbed or encapsulated in a carrier material. This is meant for either slow or rapid release depending on the requirement and is adjusted by varying permeability of the sachet material to water vapour. Its application mainly depends on the food products intended and the sensitivity of the food products to ethanol. Apart from these, various plant derivatives can be incorporated into the packaging system as antimicrobials.

7.6.3 Antioxidant Release

Antioxidants are another class of compounds used extensively in most of the oxygen-sensitive foods to improve the oxidation stability. Fish being highly rich in polyunsaturated fatty acid, are prone to oxidation. Common antioxidants used for direct food applications were BHA, BHT, etc. whose use is now not permitted in most of the food products due to its ill effects by accumulating in adipose tissue. Incorporation of natural plant extracts are also practised however it requires to use more quantity leading to influence the sensory properties. Direct incorporation of antioxidants into the packaging films and use as antioxidant is gaining more attention worldwide. However, the antioxidant compound should be able to withstand the extrusion conditions for its applications. Vitamins E and C are the common natural antioxidants, and their incorporation in polymer films to exert antioxidative effects is still at the experimental stage. Vitamin E is stable under processing conditions and has an excellent solubility in polyolefins. However, it is confirmed that, vitamin E is a less mobile antioxidant in low-density polyethylene (LDPE) than BHT, as vitamin E is a larger molecule (Wessling et al. 1998). Apart from these, natural antioxidants extracted from plant and animal substances and their use as antioxidant packaging are under experimental stages.

7.6.4 Release or Absorption of Flavours and Odours

Fish and shellfish have a typical fresh flavour, which is distinct from any food systems. Food packaging materials, particularly some plastics, may interact with these flavours, resulting in loss of flavour known as *'flavour scalping'* which affects the quality of the product. Furthermore, flavours are usually lost or degraded during various stages of processing at different temperatures or after packaging. Therefore, there is a need to replace the lost flavour constituents when scalping or degradation occurs. Flavour incorporation in packaging material might be used to minimize flavour scalping. Consumers always like to smell good flavours when they first open a food package. The applications of suitable flavour enriched packaging materials have the potential to improve the organoleptic quality of the product by emitting desirable flavours into the food and to encapsulate pleasant aromas that are released upon opening. Flavour release may also provide a means to mask off odours coming from the fish or the packaging. It is of utmost importance that the aforementioned technology should not be misused to mask the development of microbial off-odours thereby concealing the marketing of products that are below standard or even dangerous for the consumer (Nielsen 1997).

Flavour scalping, i.e. sorption of food flavours by polymeric packaging materials, may result in loss of flavour. Generally, flavour scalping is detrimental to food quality, but it could be used in a positive way to selectively absorb unwanted odours or flavours. In contrast to flavour releasing systems, flavour absorbers scavenge undesirable flavours, aromas and odour present in the package headspace. The formation of off-flavour and off-odour in fish products are mainly from the oxidation of fat and oils, leading to the formation of peroxides and their decomposition products like aldehydes, breakdown of fish proteins into amines forming alkaline compounds. Flavour absorbing systems employ cellulose triacetate, acetylated paper, citric acid, ferrous salt/ascorbate and activated carbon/clays/zeolites to absorb off-odour and off-flavour. Removal of aldehydes from package headspaces can be achieved by means of the layer Bynel IXP101 which is a HDPE master batch. Amines can be removed by reacting with acidic compounds, e.g. citric acid incorporated in polymers.

7.6.5 Time-Temperature Indicators

Food and pharmaceutical products are highly sensitive to the temperature of storage. They need to be maintained at specified temperature throughout their shelf-life to ensure its quality and safety. Frozen food products have relatively very long shelf life ranging from 6 months to 2 years. They should be stored at -18 ± 2 °C from the point of production till they are consumed. However, cold chain is broken due to many reasons like improper cold chain facilities at all the stages of food distribution, frequent power failure and regular opening and closure of freezer door at retail outlets. Failure to maintain specified temperature will indirectly affect the quality and safety of the product. It is difficult to find out whether the frozen food product has thawed at some point and then refrozen. As there is no device/method to monitor such temperature abuses, consumers will end up buying inferior quality products. At the same the producers will get bad reputation due to breakdown of cold chain which is not in their hand to maintain. The principle behind this is that as the temperature increases, biochemical and microbial reactions take place at rapid rate leading to deterioration of food. TTIs are based on either chemical, electrochemical, enzymatic, microbial or mechanical reaction leading to visible response. TTIs find its applications not only in food products, but also in pharmaceutical products to ensure better quality product to consumers. Recent research on TTI indicates that the active compound, sensitive to temperature fluctuation can be incorporated into the polymer/biodegradable film that can change the colour as temperature is abused. Indicator dyes, plant and fruit extracts containing specific pigments responsible for giving colour change with the fluctuation in the temperature are used in this.

7.6.6 Freshness Indicators

Fish production as well as fish consumption is on the rise both in the domestic and international market. Understanding the ever-increasing demand for fish, retail marketing and online marketing is flourishing across India and the price of fish is also increasing. Due to recently reported adulteration menace, consumers are always at doubt while purchasing fish. Fish being highly perishable, undergoes spoilage leading to formation of various chemicals (oxidation products and amines) which may affect the health of the consumers. The fish quality is either ensured by sensory attributes or by analytical methods. However, the analytical methods are time consuming, costly and are not real-time in nature. This has resulted in relying on sensory quality assessment to judge the quality of fish being marketed. However, sensory quality analysis is qualitative and it can be biased and hence, quality control requires rapid methods for measuring fish freshness in real-time. An intelligent packaging technology will be beneficial for this purpose. This can be achieved by using freshness indicator or spoilage indicators. Commonly developed freshness indicators are based on the reaction between the volatile compounds or other constituents generated during the process of spoilage with the indicating material. Freshness indicators provide direct product quality information resulting from microbial growth or chemical changes within a food product. Microbiological quality may be determined through reactions between indicators included within the package and microbial growth metabolites (Smolander, 2003). Normally, the freshness indicators are incorporated into the packaging film, which reacts with volatile amines and other indicating agents produced during the storage of fish and other seafoods, and the freshness is indicated by a colour change.

7.7 Studies on Functional Packaging Materials

Smart packaging includes both active and intelligent packaging systems. Active packaging refers to alternation of package atmosphere/incorporation of suitable compounds to enhance the quality and shelf life, whereas intelligent system monitors the condition of packaged food to give information regarding the quality of food. Research on development of smart packaging devices for perishables including fish is very limited in India. Many researchers are carrying out work on various aspects of smart functional packaging materials. Chemical combinations for O_2 scavenger, CO_2 emitter is optimized using GRAS chemicals which can reduce the O_2 level to 0.01% and increase the CO_2 level to >80% within 24 h, respectively (Mohan 2008). Dual-action sachet, which combines the scavenging of O_2 and emits CO_2, is also developed and found to extend the shelf life of fatty fish up to 25 days (Mohan 2008). These developed active packaging systems follows first-order reaction and extends the shelf life of fishery products significantly (Mohan 2008). Studies indicated that O_2 scavenger was very efficient in reducing oxygen concentration by 99.58% within 24 h inside the packages and found to extend the catfish steaks shelf-life up to 20 days, compared to 10 days in control air packs (Mohan et al. 2008). Studies on Seer fish indicated a shelf life extension of 20 days under O_2 scavenger compared to only 12 days for air packs and inhibited the formation of biogenic amines, especially histamine by inhibiting bacterial enzyme activity (Mohan et al. 2009a). The use of O_2 scavenger positively extended the shelf life by inhibited the formation of volatile bases, inhibiting the nucleotide degradation resulting in delayed formation of hypoxanthine, which is associated with the spoilage of fish (Mohan et al. 2009b). The use of O_2 scavenger improved the shelf life of barracuda steaks by 20 days (Remya et al. 2018) and Indian oil sardine by 15 days (Mohan et al. 2019a, b) under chilled storage. A delay in the growth of microorganisms including specific spoilage flora like *Pseudomonas* spp. and H_2S forming bacteria was observed in fishes packed with O_2 absorber by extending the lag phase which is mainly due to the effect of altered atmosphere (Mohan et al. 2010a). A shelf life of 9–10 days was observed for long tail tuna (*Thunnus tonggol*) packed under O_2 scavenger under chilled stored (Mohan et al. 2014).

Active antimicrobial packaging films prepared using chitosan incorporating ginger (*Zingiber officinale*) essential oil (GEO) was effective against foodborne pathogens (Remya et al. 2016). Keeping quality of steaks of barracuda (*Sphyraena jello*) fish improved significantly in the chitosan films with GEO (Remya et al. 2016). Antimicrobial packaging film incorporating silver nanoparticles synthesized using low and high molecular weight and other chemicals can be used effectively to control the growth of foodborne pathogens (Pankaj et al. 2017). Combination of O_2 scavenger and antimicrobial film incorporating essential oil resulted in enhanced quality retention and reduced oxidation and extended the shelf life up to 30 days in chilled storage condition (Remya et al. 2017). Combination of curry leaf essential oil and O_2 scavenger resulted in increased lag phase and reduced oxidation in *Rachycentroncanadum* and extended shelf life up to 30 days (Remya et al. 2014). Antimicrobial coating with chitosan resulted in reduced microbial growth, volatile formation, oxidation, drip loss and improved water holding capacity and improved the texture of Indian oil sardine (Mohan et al. 2012; Renuka et al. 2016). The formation of total volatile base nitrogen and trimethylamine nitrogen was less by 14.9–32.7 and 26.1–49% for different concentrations of chitosan-treated samples (Mohan et al. 2012). Biodegradable antioxidant packaging film developed using rosemary essential oil resulted in improved DPPH activity and total phenolic content (Mohan et al. 2018). Moisture absorbing system developed using aquatic weed, water hyacinth to absorb the drip formed during the storage of fish.

Similar to active packaging systems, ICAR-CIFT has also developed various intelligent packaging systems. A simple, easy to use and cheap (Only Rs 0.4 per pack equivalent to US$ 0.0055) freshness indicator is developed for indicating quality of fish and shellfishes. The effectiveness of freshness indicator is evaluated with fishes of freshwater, marine and brackish water origin and found effective, except for freshwater fishes. Studies on nanoparticle-based intelligent packaging system to develop temperature history sensor were developed in collaboration with University of Wisconsin-Madison, USA (Wang et al. 2017). Nanocomposite of chitosan and gold nanoparticles (AuNPs) was used to develop sensors that can indicate the frozen state and thermal history of foods and other temperature-sensitive products based on the visual colour change (Wang et al. 2017). A greener method used for the synthesis of Gold nanoparticle using chitosan to develop temperature history indicator to ensure the quality and safety of frozen stored perishable food and pharma products during shipment and transportation (Mohan et al. 2019a, b). Developed and characterized gold, silver and copper nanoparticles using different chemicals and biological sources of marine origin which finds application as biogenic amine and heavy metal detecting sensor. Developed paper-based colorimetric nano-biosensor strip for detection of foodborne pathogens including *E. coli* 0157:H7 and *E. coli* which reduced the detection time (Nadella et al. 2019). A detailed review on active and intelligent packaging systems is documented (Mohan et al. 2009a, b, 2010b, 2018; Biji et al. 2016).

Apart from this, the institute is also steer heading the research on developing biodegradable smart packaging materials with improved properties. Chitosan, collagen, chitosan-collagen-based films were developed for its application as wrap. PLA-based biodegradable packaging material with improved mechanical properties and heat sealability is developed. Seaweed based functional and edible films developed exhibited good sealing and antioxidant properties and can be used as novel packaging material in food industry as a sachet/pouch/bag for seasoning powder for instant noodles, instant coffee/tea, etc. Continued research and development is needed for enhancing the efficiency of smart packaging systems developed. Collaboration with other research institutes is the need of the hour to fine tune and upscale the developed smart packaging technologies, validate properties of smart packaging devices developed in field condition and commercialization.

7.8 Conclusion

Apart from proper handling, there is a need to adopt advanced packaging technologies, particularly cost-effective smart packaging to overcome this problem. Although advanced packaging technologies like vacuum and modified atmosphere packaging technologies are available, their adoption in middle- and low-income countries are very insignificant due to its high cost and its maintenance. Apart from reducing post-harvest losses, providing quality and safe fish products without the use of any chemical preservative is a challenge world is facing today. Advanced, low-cost packaging options to enhance the quality, shelf-life and safety are the need of the hour. Advancements in the biodegradable packaging material with functional attributes will continue to progress which brings new concepts and opportunities to enhance the quality and safety of perishable commodities. Adoption of these functional packaging materials will bring new avenues to entrepreneurs and industry persons to enhance their marketing capabilities as the consumers will get the trust on such products which use functional packaging materials to show that these products are better compared to conventional ones.

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Edible Films and Coatings: Major Challenges and Potential Applications in Food Packaging. A Review

8

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Abstract

Petroleum-based plastics, largely used in food packaging, have raised a great number of health and environmental issues mainly due to their non-renewable source. Biopolymers-based films and coatings designed to preserve the food quality have attracted the attention of many researchers since they are made from renewable resources, and could in addition carry bioactive compounds like antimicrobials and antioxidants that lead to prolong the shelf life of food. However, to be adequately used in food packaging, they must meet a certain number of functional properties like mechanical resistance and gas permeability. This work systematically discusses the most significant functional characteristics of edible films and coatings like mechanical, gas barrier and water vapor permeability, solubility, and organoleptic properties as well as their bioactive characteristics. It also highlights their potential applications and limits in fruits and vegetables, meat products, cheese, and sea foods. The challenges faced so far, and the prospects for their progress and development are also discussed.

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8.1 Introduction

Food preservation aims to increase the storage life of food and preserve their quality. Several methods have therefore been developed. Classical empirical techniques such as cooking, drying, or salting, and others such as freezing, canning, pasteurization, and packaging have been commonly used (Augusto et al. 2018). The role of food packaging is to contain food and protect it from external contaminations. It constitutes a physical barrier against mechanical shocks, transfers of matter and energy, and against microorganisms (Berk 2018).

In the early twentieth century, with polyethylene's invention, food transportation and storage was revolutionized. Plastic packaging has since occupied an important place in the food industry because of its practicability, low cost, and functionality. Therefore, global production of plastic packaging exceeded 150 million in 2015 (Groh et al. 2019). However, a number of environmental concerns have been raised regarding the continued use of plastic materials in food packaging, considering the fact that they are non-biodegradable, almost non-recyclable, and have a very limited shelf life, resulting in large amounts of waste that have huge environmental impacts (Hahladakis et al. 2018). On the other side, toxic and undesirable substances such as monomers, synthetic antioxidants, chemicals, etc., could be transmitted once in contact with food (Bolívar-Monsalve et al. 2019). For these reasons, there is a major interest in the development of new packaging materials, biodegradable, non-contaminating, made from renewable and recyclable resources.

In this context, films and coatings made from biopolymers have attracted the attention of many researchers as an alternative to petroleum-based plastics (Menezes n.d.; Umaraw and Verma 2017; Rojas-Graü et al. 2009; Han 2005). Biodegradable films and coatings are described as thin films or coating solutions (Fig. 8.1) made from biopolymers (proteins, polysaccharides, etc.) and are applied as primary food packaging providing a barrier to factors such as moisture, gases, and vapors, and improving therefore their quality (Huber and Embuscado 2009).

In addition, these biopolymers-based films and coatings (BFC) could also carry bioactive compounds, such as antimicrobial agents and antioxidants, contributing in this case to improve the food shelf life (Quezada-Gallo 2009; Salgado et al. 2015; Raybaudi-Massilia et al. 2016; Atarés and Chiralt 2016; Ganiari et al. 2017).

However, to be used effectively in food packaging, BFC must fulfill several functional properties such as mechanical, water, and gas permeability, as well as organoleptic and antimicrobial properties (Fig. 8.2).

This work is an overview aiming to present and analyze the main findings of recent studies with regard to the functional properties of BFC and their potential food applications.

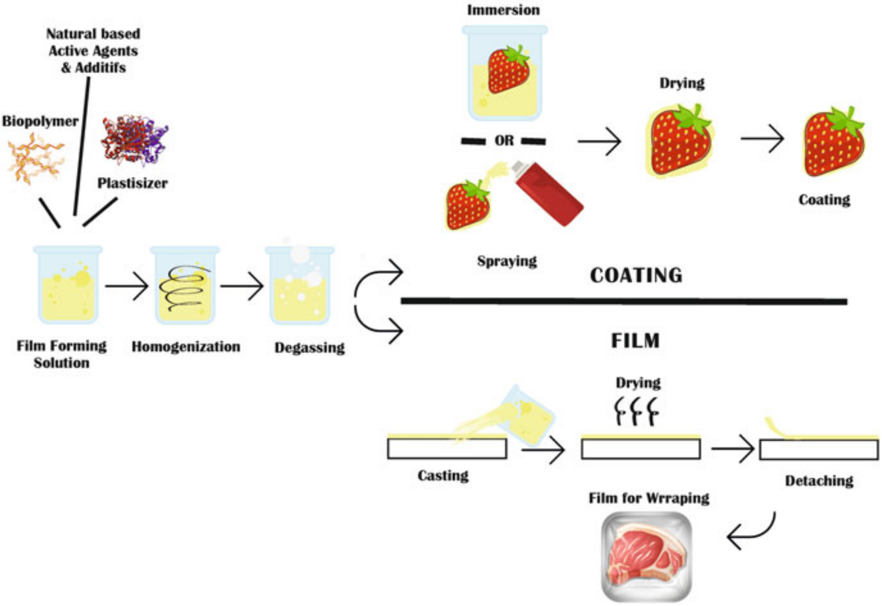

Fig. 8.1 Development of biopolymers based films and coatings

8.2 Functional Properties of Biopolymers-Based Films and Coatings

8.2.1 Mechanical Properties

To be efficient, BFC used in food packaging must be mechanically strong enough to protect the product from any abrasion and maintain its integrity during manipulation, storage, and transportation (Wihodo and Moraru 2013). The mechanical resistance of films is determined mainly by their tensile strength (TS) and elongation at break (EB) values.

The improvement of films' mechanical properties depends on the biopolymer nature itself, the additional use of plasticizers, and the control of film manufacturing parameters such as the type of process used, environmental humidity, speed, and temperature of drying or cooling (Debeaufort et al. 1998).

According to Jiménez et al. (2012), the solvent evaporation step for films manufactured by wet process is as important as the cooling step in the dry process. Cho and Rhee (2002) investigated the impact of the environmental humidity on the films' mechanical properties and showed that hydrophilic films tend to absorb moisture more easily, thereby increasing the plasticizing effect of water leading to reduced TS.

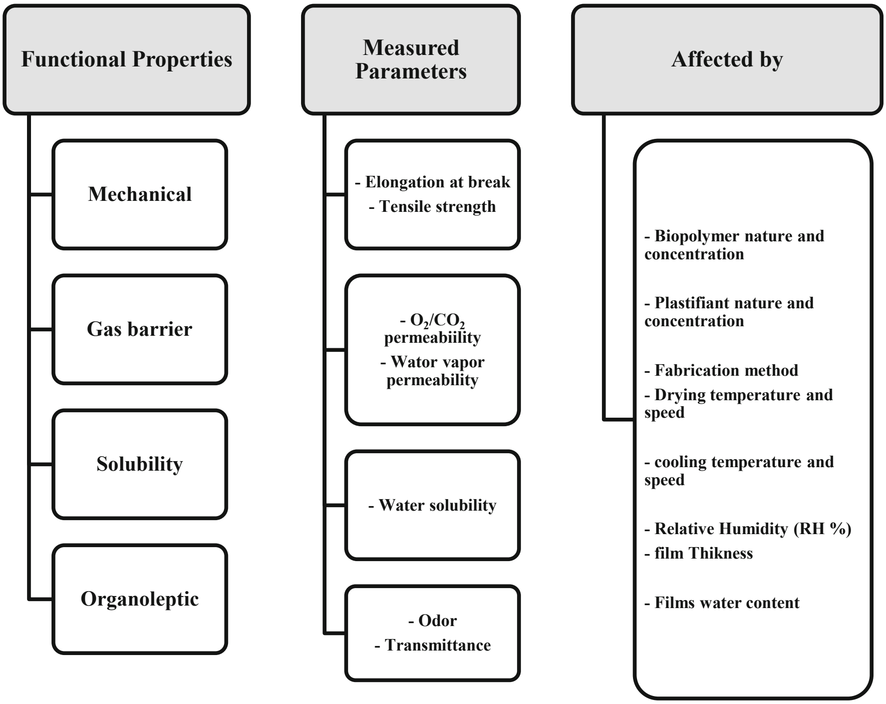

Fig. 8.2 Functional properties of biopolymers-based films and coatings

The use of plasticizers has a considerable influence on the mechanical properties of films. The presence of a plasticizer on the film matrix increases the mobility of polymer chains by increasing the intermolecular space, leading to higher EB and lower TS levels (Vieira et al. 2011).

It was demonstrated that a double increase of glycerol results in a large increase of elongation at break (76% instead of 17%) and a threefold decrease of TS values (Butler et al. 1996). It should be noted that mechanical properties are also affected by the type of plasticizer and molar mass modifications of biopolymers (Cao et al. 2018). Sothornvit and Krochta (2005) revealed that a decrease in molar mass creates more terminal groups and free volumes in polymers, giving films with higher elongation at break levels. In this sense, Aitboulahsen et al. (2020a) showed that films made from sorbitol as a plasticizer displayed higher TS than films made from glycerol for three different biopolymer-based films (gelatin, pectin, and starch).

Table 8.1 compares TS and EB values of films made with bio- and synthetic polymers. Synthetic polymers have comparable TS levels to that of films made with polysaccharides but higher values of elongation at break (up to 1000 %). However, since many factors are involved, results cannot be compared easily.

Table 8.1 Mechanical properties of edible and/or biodegradable films (~25°C, 50% HR)

Polymer	Tensile strength (MPa)	Elongation at break (%)	Reference
Cellulose	44–65	10–50	Saremnezhad et al. (2011)
Chitosan	10–100	20–80	Saremnezhad et al. (2011)
Type A gelatin	25–85	7–22	Mark (1999)
Type B gelatin	28–140	7–12	Mark (1999)
Starch	35–46	1.7–3.4	Mark (1999); Saremnezhad et al. (2011)
Soy protein	3.7–4.5	152–160	Saremnezhad et al. (2011)
Whey protein	2.5–3	15–18	Saremnezhad et al. (2011)
Corn zein	3–4	50–120	Padua and Wang (2002)
Low-density Polyethylene (LDPE)	9–20	100–1200	Mark (1999)
High-density polyethylene (HDPE)	10–60	400–1800	Mark (1999)

8.2.2 Gas Barrier and Water Vapor Properties

Oxygen fixation in food products is irreversible and may lead to oxidative rancidity; its absence, however, could result in anaerobiosis (Yano 1990). Gas barrier properties of BFC are therefore of great importance. They should act by protecting the quality of food susceptible to oxidation (rancidity, loss of vitamins) and controlling respiratory exchanges of fruits and vegetables (Zahedi 2019).

Permeability is defined as permeants transmission through materials (Han 2005). The fundamental principle of permeation is based on the adsorption/dissolution-diffusion/desorption mechanism.

In absence of pores, defects, and membrane perforations, the permeability P is equal to the product of diffusion coefficient D (representing permeants mobility in the polymer) and of solubility coefficient (representing the concentration of permeants in the film at equilibrium with the external pressure).

$P = D*S$ (Colak 2014)

In this process, gases such as O_2 and CO_2 cross the biopolymer matrix and are therefore transferred to the external environment or the reverse and lead to changes in food safety and organoleptic characteristics of food (Han 2005).

According to Debeaufort et al. (1998), edible films made with proteins or polysaccharides have generally good oxygen barrier properties particularly under conditions of low humidity; nevertheless, they are often lower to those of conventional synthetic films such as polyethylene.

Due to their linear structure and high percentage of amino acid groups, films made with corn zein, wheat gluten, soy, or wheat protein are characterized with higher permeability to oxygen than the ones made with polysaccharides (Wu et al. 2002). The same authors reported that gas permeability properties of starch or lipid films affected the shelf life of the packed food.

The plasticizer nature and concentration also affected the oxygen permeability of BFC.

Water vapor permeability (WVP) can be defined as the rate of water vapor transmission by unit area of a giving material with known thickness and by difference in vapor pressure between two surfaces, under known temperature and humidity conditions. It is directly related to environmental conditions and to the amount of –OH groups in the molecule (Henrique et al. 2007).

Water vapor permeability (WVP) of BFC was investigated by several authors (Gennadios et al. 1994; Debeaufort and Voilley 1994; McHugh et al. 1994; Bertuzzi et al. 2007; Al-Hassan and Norziah 2012; Aitboulahsen et al. 2020a). It depends on various factors such as molecules solubility on the film matrix, hydrophobic/hydrophilic nature of biopolymers, their structure, polymeric chain mobility, interactions between polymers functional groups, hydrophobic/hydrophilic and crystalline/amorphous ratios, type and concentration of plasticizer, film thickness and ambient conditions (temperature, relative humidity…) (Debeaufort and Voilley 1994; McHugh et al. 1994; Pérez-Gago and Krochta 1999).

The addition of lipidic, hydrophobic compounds can be an effective approach to improve WVP of BFC. The low polarity of lipids and their ability to form dense and well-structured molecular matrices reduces water mobility (Debeaufort and Voilley 2009). Regarding the plasticizer effect, the use of polyols, especially glycerol and sorbitol, improves films flexibility to the detriment of water vapor barrier (Haq et al. 2014). The same authors observed that WVP increases with glycerol concentration increase for gum-based films. In contrast, sorbitol was proved better than glycerol for obtaining less permeable films to water vapor (Razavi et al. 2015).

On the other hand, incorporation of hydrophobic substances in BFC matrix such as essential oils (EOs) would improve water vapor barrier properties. Basil seed gum incorporated with oregano EO allowed the decrease of WVP values due to the interference of oil globules on the transmission of water molecules in the coating matrix (Gahruie et al. 2017).

Table 8.2 shows gas and water vapor property values of edible and synthetic films and coatings. Starch and protein films are generally highly permeable to water vapor but less permeable to gases. It is therefore necessary to optimize the barrier properties according to food product requirements (Wihodo and Moraru 2013).

8.2.3 Thickness

Mechanical and barrier properties of BFC are directly influenced by their thickness (Zahedi 2019). Biopolymers-based films and coatings thickness depends on many factors such as the production process and the concentration and type of components, particularly, plasticizers (Zahedi 2019). Gheribi et al. (2018) showed that glycerol addition as a plasticizer can absorb a great deal of water resulting in inflated films with high thickness.

Razavi et al. (2015) observed that sage seed gum films supplemented with sorbitol were thicker than those containing added glycerol. Density difference

Table 8.2 Water vapor and gas permeability values of some bio- and synthetic polymers (Krochta and de Mulder-Johnson 1997; Embuscado and Huber 2009)

Materials	WVP (10^{-11} g/m.s. Pa) ~38 °C, 90/0% HR	PO_2 (10^{-17} g/m.s. Pa) ~25 °C, 0–50% HR
Methylcellulose	8.7	15–150
Starch	17.5–25.7	15–150
Gelatin	16	1.5–15
Chitosan (2%)	3.6–4.9	15–150
Zein	53-89	15–150
Gluten	0.1–10	1.5–15
Whey protein	71	1.5–15
High-density polyethylene HDPE	0.02	4
Low-density polyethylene LDPE	0.09	14.3
Polyethylene terephthalate PET	0.28	0.08

between the different phases of the films and emulsified components interactions may modify thickness (Razavi et al. 2015).

According to Gahruie et al. (2017), thyme EO incorporation in basil seed gum films increases thickness. This may be explained by the presence of lipid molecules between polysaccharide chains which inhibits the development of ordered and compact structure, dilating film matrix (Haq et al. 2016).

8.2.4 Solubility

The majority of BFC are soluble in water (Menezes n.d.). This property is of great interest through its applicability on foodstuffs with different compositions and for other technological purposes. Films solubility in water should be controlled depending on food product and according to the intended technological purpose. Indeed, ready-to-eat semi-finished food products require films with high solubility. In contrast, for packaging of high water activity products, films should be less soluble. Inversely, packaging that should be dissolved before product consumption (cooking, infusion) should be highly soluble. To optimize packages' water solubility, the use of insoluble lipids and proteins and some other hydrophobic components was investigated in order to preserve films from inflation or disaggregation (Debeaufort and Voilley 2007). Composite films allow better resistance to water and polymers crosslinking. Vachon et al. (2000) have successfully reduced films solubility to more than 75% favoring reticulation by irradiation treatment.

Rompothi et al. (2017) observed that concentration increase of plasticizer increases solubility, whereas concentration increase of the biopolymer (starch) decreases solubility. They also noted that glycerol gives less soluble films than sorbitol. According to the same authors, this is due to plasticizer migration which was difficult when film matrix was more compact with high proportion of cohesive forces between starch chains.

8.2.5 Organoleptic Properties

Organoleptic neutrality is also important for BFC. Transparency/opacity, smell, taste, brightness, etc. are important organoleptic properties that should be controlled. Furthermore, compatibility of these properties with food matrix is a parameter that must be taken into account (Fernández-Pan et al. 2011).

Generally, protein or polysaccharide films are more neutral than lipid ones, which are contrarily more opaque and sliding with light wax taste (Krochta 2010). Additives addition, especially EOs which plays a major role as antimicrobial agent may influence significantly the smell and taste of films and consequently those of the food (Atarés and Chiralt 2016). Khwaldia et al. (2004) showed that edible films made with milk proteins result in a bad taste during storage due to lipid oxidation products, Maillard reaction, and vitamins degradation.

Films' optical properties are also of paramount importance as they have direct impact on product appearance and acceptability by the consumer (Ozdemir and Floros 2008).

Kaya et al. (2018) have shown that incorporation of seed oil and dried fruits extract in film matrix made with chitosan decreases film transparency.

Nisar et al. (2018) also observed a decrease in films' transparency with clove EO addition in pectin films and reported that this may be due to phenolic components which can absorb light at different wavelengths with a natural yellowish color attributed to lipids or EOs.

8.2.6 Antimicrobial Properties

Antimicrobial substances can be added to BFC to confer them antimicrobial properties inhibiting microbes' growth on food surfaces. These incorporated antimicrobial agents are released in a progressive and controlled manner maintaining low microbial counts throughout the storage period (Bolívar-Monsalve et al. 2019; Sánchez-González et al. 2011; Janes and Dai 2012; Espitia et al. 2016; Avila-Sosa et al. 2016; López et al. 2007).

Table 8.3 shows the inhibitory effect of some antimicrobial films on pathogens. Lysozyme incorporation in chitosan-based films was effective to reduce *Escherichia coli* and *Streptococcus faecalis* growth levels (Park et al. 2004). Chitosan-based coatings supplemented with potassium sorbate and nisin showed inhibitory action against *Escherichia coli*, *Staphylococcus aureus*, *Salmonella typhimurium*, *Listeria monocytogenes,* and *Bacillus cereus* (Pranoto et al. 2005).

Hettiarachchy and Satchithanandam (n.d.) incorporated organic acids in soy proteins films and demonstrated their antimicrobial effect against *Listeria monocytogens*, *Salmonella gaminara*, and *Escherichia coli O157:H7*.

The antimicrobial effect of BFC containing EOs was widely investigated (Avila-Sosa et al. 2016). Rojas-Graü et al. (2007a, b) examined the antimicrobial properties of films incorporated with various EOs. The most effective was carvacrol followed by oregano, lemon, lemongrass, and cinnamon. Ravishankar et al. (2009) have

Table 8.3 Antimicrobial activity of biopolymers-based films and coatings containing antimicrobial agents

Composition of the film	Antimicrobial agent	Targeted microorganisms	References
Whey proteins isolates	Essential oils: Oregano/rosemary/garlic	*Escherichia coli* O157 : H7 *Staphylococcus Aureus* *Salmonella* enteritidis *Listeria monocytogenes*	Seydim and Sarikus (2006)
Chitosan	Nisin Potassium sorbate	*Escherichia coli* *Salmonella typhimurium* *Staphylococcus aureus* *Bacillus cereus* *Listeria monocytogenes*	Pranoto et al. (2005)
Pectin—apple puree	Essential oils: Oregano/lemongrass/cinnamon	*Escherichia coli* O157 : H7	Rojas-Graü et al. (2007a, b)
Whey proteins isolates	Lactoperoxidase	*Salmonella enterica and Escherichia coli O157:H7*	Min et al. (2006)
Sodium alginate	Castor oil	*Staphylococcus aureus Bacillus Subtilis, Escherichia coli, and Salmonella typhimurium*	Abdel Aziz Mohamed et al. (2018)
Starch	Methanolic extracts of *Hibiscus sabdariffa*	*Listeria monocytogenes*	Cruz-Gálvez et al. (2018)

shown that chicken breast fillet and ham wrapped with pectin-apple puree films supplemented with different concentrations of cinnamaldehyde or carvacrol have significantly reduced *Salmonella enteritidis*, *Escherichia coli O157: H7,* and *Listeria monocytogenes* growth levels.

Basil seed gum films containing oregano EO produced by Gahruie et al. (2017) showed significant antimicrobial activity against *Escherichia coli, Salmonella typhimurium, Pseudomonas aeruginosa, Staphylococcus aureus,* and *Bacillus cereus*.

Lin and Zhao (2007) and Ozdemir and Floros (2008) showed that EOs diffusion on films matrix is influenced by many factors such as biopolymer nature, additives, manufacturing process, pH and water activity of the food and storage time and temperature.

Due to its film-forming and antimicrobial properties, the chitosan effect on food shelf life was widely investigated. Coma et al. (2002) and Ponce et al. (2008) reported its inhibitory effect against *Listeria monocytogenes* and Maqbool et al. (2011) proved the efficacy of chitosan-based coatings in slowing the growth of *Fusarium* spp., *Colletotrichum musae,* and *Lasiodiplodia theobromae* when preserving bananas. It has been proven that the use of these films and coatings improved fruits and vegetables shelf life by inhibiting microorganisms' growth, reducing ethylene production, increasing carbon dioxide concentration, and by reducing oxygen levels (Geraldine et al. 2008; Lazaridou and Biliaderis 2002).

8.3 Films and Coatings Applications on Food Products

During storage and distribution, food products are subject to dynamic changes, mainly due to interactions between them and their surrounding environment that adversely affect their quality and lead to deterioration. Several formulations of BFC made from different biopolymers, additives, and their mixtures have been tested and applied to food products such as fruits and vegetables, cereals and dried fruits, meats, poultry or seafood, cheese, fresh food, salted, frozen and processed, etc…

In the following section, an overview on the various applications of BFC on food products will be addressed.

8.3.1 Applications in Fruits and Vegetables

Fruits and vegetables are usually altered after harvest, during ripening and storage because of gas exchange, respiration, transpiration, and microorganisms’ attacks. Edible films and coatings applied to fruit and vegetables aim to reduce the respiratory rate, water loss, microbial degradation, and thus help to preserve their quality (Yousuf and Qadri 2020). Besides, the incorporation of antimicrobial agents such as plant extracts and EOs prevents harmful microbial growth, particularly molds, and helps improve the shelf life of fruits and vegetables (Saxena et al. 2020). In this context, some proteins and polysaccharides-based coatings have been developed to control the ripening of fruits and vegetables. Their selective permeability creates a changed internal atmosphere that helps to sustain a reduced respiratory rate and thus slows down the metabolism of fruit and vegetables after harvesting, thus enhancing their shelf life (Yousuf and Qadri 2020). In this regard, a recent study has shown that the application of alginate-based coating with rhubarb extract has contributed to a substantial reduction in the respiration rate of peach fruit (Li et al. 2019). Similarly, a polysaccharide-based coating applied to potatoes was an efficient oxygen barrier and decreased respiration during storage (Wu 2019).

Applying films and coatings to fruit and vegetables should retain firmness after harvesting and minimize water and weight loss. Accordingly, Correa-Pacheco et al. (2021) were able to preserve the firmness of green pepper fruits, during 12 days of storage at 10 ± 1 °C, using chitosan nanoparticles-based coating.

Aitboulahsen et al. (2018) and Pinzon et al. (2020) also demonstrated the positive effect of the coating on the texture of strawberries during storage, thus addressing the problem of cell wall degradation of strawberries during storage. Kozlu and Elmacı (2020) obtained similar results for mandarin fruits coated with a quince seed mucilage-based coating.

The incorporation of active substances, such as antioxidants, helps to delay post-harvest browning of fruits and vegetables, by chemical reduction of quinones to colorless orthodiphenol reducing agents, acting in the enzymatic browning process, which consists of the oxidation of phenolic substrates to colored orthoquinones (Saxena et al. 2020).

Browning can also be inhibited in an atmosphere containing less than 1 kPa of oxygen (Gorny et al. 2002), for this, packing fresh fruits and vegetables with BFC, whether or not containing antioxidants can be a better way to prevent oxygen diffusion due to mechanical damage during handling, transport, or storage. These films and coatings improve the oxygen and light barrier, prevent polyphenol oxidase (PPO) contact with oxygen, and maintain a stable amount of ascorbic acid (Lin and Zhao 2007).

El-Mogy et al. (2020) concluded that artichoke bottoms coated with a Cordiamyxa gum coating incorporated with calcium dichloride ($CaCl_2$ and ascorbic acid prolong the shelf life of fresh artichoke bottoms by delaying their browning and improving their texture compared to control fruits. Wang and Gao (2013) obtained the same results on strawberries coated with chitosan. The authors reported a decrease in the weight loss and the activity of PPO, as well as a stable content of anthocyanins, flavonoids, and total phenolics. A recent study carried out on freshly cut lettuce claimed that coating with chitosan is an effective method to prevent enzymatic browning and therefore extend the shelf life of fruits and vegetables (Li et al. 2021).

On the other hand, the damage of fruit, vegetable, or plant tissue establishes ideal conditions for microbial growth (Chen et al. 2021). The applications of BFC containing antimicrobial agents have been largely used to overcome this problem (Azarakhsh et al. 2014; Shahbazi 2018; Hu et al. 2020; Meindrawan et al. 2020; Arabpoor et al. 2021).

Maqbool et al. (2011) demonstrated that the incorporation of lemongrass and cinnamon EO in Arabic gum-based coatings extended the banana's shelf life up to 33 days, and allowed to control anthracnose caused by *Colletotrichum spp.* Figure 8.3 shows the evolution of the hygienic quality of strawberries coated with gelatin incorporated with pennyroyal EO. In this study, Aitboulahsen et al. (2018) showed that the bioactive coating used decreased fungal contamination of strawberries during storage and thus increased their shelf life. Table 8.4 summarizes the most relevant applications of BFCon fruits and vegetables.

8.3.2 Applications in Cheese

Cheese is an ancient food product that makes part of humans' regular diet, due to its composition characterized by high amount of protein, calcium, minerals, and vitamins. The intensive growth of yeasts, molds, and undesirable bacteria on cheese surfaces can considerably reduce its quality. Biopolymers-based films and coatings have been largely used for preserving the quality of cheeses (Duan et al. 2007; Kuorwel et al. 2013; Di Pierro et al. 2011; Cerqueira et al. 2010; Oliveira et al. 2017).

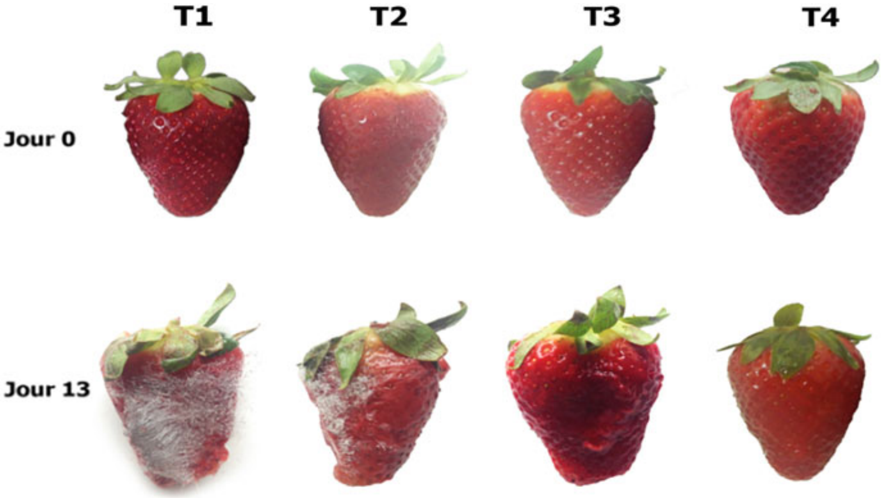

Fig. 8.3 Appearance change of strawberries coated with a gelatin coating incorporated by pennyroyal essential oil (MEO) or not during 13 days of storage at 4 °C. (T1: Control; T2: Gelatin coating + 0% MEO; T3: Gelatin Coating + 0.5% MEO; T4: Gelatin Coating + 1% MEO) (Aitboulahsen et al. 2018)

Low moisture Mozzarella slices coated with chitosan incorporated with lysozyme allowed a delay of microbial growth of *Escherichia coli, Pseudomonas fluorescens, and Listeria monocytogenes* after 14 days of storage at 10 °C (Duan et al. 2007). For ricotta without the rind, the coating based on whey and chitosan extended cheese shelf life up to 30 days (Di Pierro et al. 2011). The same type of cheese was coated with a galactomannan-based coating containing nisin and showed a significant growth reduction of *Listeria monocytogenes* inoculated intentionally on the cheese surface, compared to uncoated control (Martins et al. 2010). According to Kuorwel et al. (2013), the starch-based coating incorporated with linalool, carvacrol, and thymol was effective against the development of *Aspergillus niger* on cheddar's surface during storage. However, the use of EOs can produce strong odors and aromas influencing the sensorial quality of the cheese (Yangilar 2016). More recent studies summarized in Table 8.5 also showed the effects of bioactive films and coatings on sensory characteristics of cheeses such as color, odor, flavor, and taste, as well as on the development of harmful microorganisms during the ripening process.

8.3.3 Applications in Meat

Several studies have demonstrated the effectiveness of BFC in preserving the quality of meat and poultry products (Guo et al. 2014; Shin et al. 2017; Vital et al. 2018; Saricaoglu et al. 2018; Souza et al. 2019; Bolívar-Monsalve et al. 2019). Gallego

Table 8.4 Recent applications of biopolymers-based films and coatings on fruits and vegetables

Fruit/ vegetable	Biopolymers	Additives/active agents	Application method	Storage conditions	Major findings	References
Peach fruit	Chitosan	Chlorogenic acid	Immersion for 2 min	Packed in unsealed polyethylene bags and stored for 8days at 20 °C with 80–90% RH	Antioxidant activity Preservation of physicochemical characteristics	Jiao et al. (2019)
Papaya fruit	Chitosan	*Rutagraveolens L* essential oil	Immersion for 2 min, and air-drying for 1 h at room temperature	Stored at 20 °C ± 1 °C and 88% RH for 12 days	Antifungal activity (inhibition of *Colletotrichum gloeosporioides* growth)	Peralta-Ruiz et al. (2020)
Guava fruit	Chayotextle starch and resistant starch	Ascorbic acid	Dipping for 15 s, draining and drying at room temperature	Packed in polypropylene plastic trays with a perforated cover at 4 °C and 65% RH	Delay ofmaturation changes Preservation of organoleptic characteristics (firmness and color)	Martínez-Ortiz et al. (2019)
Orange fruit	Aloe vera gel	Salicylic acid	Immersion for 5 min at 22 °C, drying at room temperature for 2 h	4 ± 1 °C and 80 ± 5% RH and transfer of 4 samples to 25 °C for 1 day	Antimicrobial activity Amelioration of chilling injury	Rasouli et al. (2019)
Strawberry	Pullulan	Cinnamon essential oil	Immersion for 60 s, drying at room temperature for 4 h	20 °C ± 2 °C and 70–75% RH for 6 day	Antimicrobial activity Prolongation of the shelf life	Chu et al. (2020)
Cherry fruit	Nano-chitosan	*Eryngium campestre L.* essential oil	Immersion for 3 min and drying at room T°C	Packed in disposable polypropylene containers and stored in dark at a 4 ± 1 °C/70% RH	Antimicrobial and antioxidant activity Improvement of physicochemical characteristics	Arabpoor et al. (2021)
Mandarin fruit	Carboxymethyl cellulose			5 ± 1 °C for 30 days	Preservation of membrane integrity	Ali et al. (2021)

(continued)

Table 8.4 (continued)

Fruit/ vegetable	Biopolymers	Additives/active agents	Application method	Storage conditions	Major findings	References
			Dipping for 3 min, drying at room temperature		Improvement of sensory characteristics	
Potato	Cactus *Opuntia dillenii*		Dipping for 3 min and draining the excess	Packed in racks at 5 °C for 5 days	Extension of shelf life (suppression of browning, weight loss, and microbial growth) Preservation of total sugars content	Wu (2019)
Artichoke	*Cordiamyxa*gum	Calcium dichloride ($CaCl_2$) and ascorbic acid	Dipping for 5 min, drying under sterile laminar flow hood at ambient conditions	Packed in polypropylene trays, thermally sealed by the stretch film and stored at 2 °C and 95% RH for 9 days	Antimicrobial activity and antibrowning activity	El-Mogy et al. (2020)
Cherry tomato	Protein hydrolysate		Dipping for 3 min and air-drying at room temperature	Packed in plastic trays at 21 °C and chilled stored 4 °C for 45 days	Inhibition of the proliferation of molds and yeasts	de da Costa et al. (2020)
Persimmon fruit	Gumarabic		Dipping for 3 min, drying for 2 h at 25 °C	Packed in clamshell clear PET boxes, and kept at 20 ± 1 °C with 80 ± 2% RH for 20 days	Reduction of weight loss, membrane leakage, and fruit softening Preservation of physicochemical characteristics	Saleem et al. (2020)
Tomato	Rice bran wax		Dipping 2–3 min, drying under the fan for about 3–5 h	32.7–34.4 °C and RH of 57.5–88.3%	Controlling spoilage of tomatoes until 27 days	Abhirami et al. (2020)
Pomegranate fruit	Chitosan	Malic acid (MA) and oxalic acid (OA)	Immersion for 2 min and drying at 20 ± 1 °C	Cold storage at 2 ± 1 °C with 80–90% RH for 120 days	Antioxidant and antibrowning activity	Ehteshami et al. (2020)

Apple	Fenugreek and flax polysaccharides		Dipping for 1 min, twisting and air-drying for 20 min	20 °C ± 5 with relative humidity 80–85%	Delaying the respiration rate and inhibiting the ethylene production Preservation of quality attributes	Rashid et al. (2020)
Carrots	Carboxymethyl cellulose/ candelilla wax	Ascorbic acid	Dipping for 1 min, and air-drying for 1 h	Placed in sterile plastic vessels overwrapped with a perforated PE foil, and stored at 5 ± 1 °C and ~70% RH for 21 days	Preservation of fresh characteristics up to 21 days of cold storage	Kowalczyk et al. (2020)
Mango	Chitosan	Lactoperoxidase	Dipping	18 °C and 60% RH	Antifungal activity	Mohamed et al. (2020a, b)
Banana	Cassava starch/ carboxy methyl cellulose	Lactic acid bacteria	Wrapping with the developed film	30 °C and 40% RH for 7 days	Antibrowning activity	Li et al. (2020)
Lettuce	Chitosan		Sprayed by both sides air-drying for 20 min at 17 °C	Packing into low-density polyethylene bags and stored at 4 °C for 15 days	Improving the hygienic quality preservation of chlorophyll levels, increasing the total phenolics, flavonoids content, and antioxidant activity	Fasciglione et al. (2020)
Cucumber	Chitosan, Carnauba Wax	Oregano essential oil	Manual application with brushes and drying with forced air at 25 °C for 10 min	Stored on polypropylene trays at 10 °C and 90% RH for 15 days	Antimicrobial activity Reduction of weight loss	Gutiérrez-Pacheco et al. (2020)

(continued)

Table 8.4 (continued)

Fruit/ vegetable	Biopolymers	Additives/active agents	Application method	Storage conditions	Major findings	References
Eggplant	Chitosan		Immersion for 5 min and air drying	Packed in perforated plastic baskets and covered with low-density polyethylene film, and stored at 10 ± 2 °C	Preservation of overall quality attributes and sensory acceptance	Sharma et al. (2021)
Avocado	Sodium alginate	*Meyerozyma caribbica* yeast	Dipping for 1 min and drying for 1 h (25 °C, 45% RH)	15 days storage	Prevention of anthracnose reduction of weight loss	Iñiguez-Moreno et al. (2020)

Table 8.5 Recent applications of biopolymers-based films and coatings on meat products

Meat product	Biopolymers	Additives/active agents	Application method	Storage conditions	Major findings	References
Chevon sausages	Calcium alginate/ Maltodextrin	*Terminalia arjuna*	Individually enclosing	6 units packed in low-density polyethylene pouches and stored at (4 ± 1 °C)	Antimicrobial activity control of lipid oxidation and storage changes	Kalem et al. (2018)
Beefloins	Chitosan	Cumin essential oil	Wrapping	Packed in polyethylene pouches, stored at 3 ± 0.2 °C for 21 days	Shelf life extension control of foodborne pathogens	Dini et al. (2020)
Raw beef meat	Pectin/fish gelatin	Olive antioxidants hydroxytyrosol and 3,4-dihydroxy phenyl glycol	Wrapping	Stored at 4 °C for 6–7 days	Delaying the lipid oxidation	Bermúdez-Oria et al. (2019)
Chicken breast	Semi-refined κ-carrageenan	Water extract of germinated fenugreek seeds	Wrapping and heat sealing	Stored at 5 °C for 7 days	Shelf life extension 6 days light-barrier films	Farhan and Hani (2020)
Fresh pork	Chitosan/gelatin	Nisin and grape seed extract	Immersion in coating solutions for 30 s, and air-drying	Packed in plastic trays at 4 °C, with light exposure	Shelf life extension Prevention of lipid and protein oxidation inhibition of microbial growth	Xiong et al. (2020)
Chilled black pork tender loin	Curdlan/polyvinyl alcohol/	Thyme essential oil	Wrapping	Stored at 4 °C for 20 days	Shelf life extension for up to 10 days	Zhang et al. (2020)
Strips of beef loins	Chitosan		Immersion for 5 s	Stored at 4 ± 1 °C	Inhibition of the growth of *Staphylococcus aureus*	Duran and Kahve (2020)

(continued)

Table 8.5 (continued)

Meat product	Biopolymers	Additives/active agents	Application method	Storage conditions	Major findings	References
Chicken nuggets	*Manihotesculenta* starch/ carrageenan	Anise, caraway, and nutmeg essential oils	Overwrapping	Stored at 4 ± 1 °C	Antioxidant and antimicrobial activity with well sensorial acceptance	Bharti et al. (2020)
Pork patties	Chitosan	Clove essential oil and nisin	Wrapping	Placed in plastic boxes and storedat 4 ± 2 °C for up to 15 days	Shelf life extension for 12 days instead of 6 days antioxidant and antimicrobial activity	Venkatachalam and Lekjing (2020)
Turkey meat	Gelatin/chitosan	*Ferulago angulate* essential oil	Wrapping	Stored at 4 °C for 15 days	Inhibition of total viable count, *Staphylococcus aureus* and coliform count	Naseri et al. (2020)
Lamb meat	Alginate	Thyme and garlic essential oils	Coating	Packed in an individual polystyrene tray over-wrapped with permeable oxygen film and stored between 2 °C and 4 °C under light exposure	Reducing lipid oxidation color maintenance	Guerrero et al. (2020)
Ground beef	Starch	Red cabbage extract and sweet whey	Wrapping	Stored at 4 °C ± 1 °C for 4 days	Preservation of the overall quality	Sanches et al. (2021)
Harbin red sausage	Chitosan		Immersion for 30 s and drying for ½ h	12 h at room temperature	Improving storage stability slowing down the growth of aerobic bacteria and lactic acid bacteria	Dong et al. (2020)
Fresh ostrich meat	QodumeShirazi seed mucilage-	Lavender essential oil	Immersion for 1 min	Refrigerated storage	Shelf life extension preservation of sensorial characteristics	Heydari et al. (2020)

Turkey filets	Chitosan	*Zataria Multiflora Boiss* and *Bunium persicum Boiss* essential oils	Immersion	Kept in sterile bags during the storage at 4 ± 1 °C for 18 days	Prolongation of shelf life to 9 days reduction of about 3 log CFU/g in *S. enteritidis* population and about 2 log CFU/g in *L. monocytogenes*	Keykhosravy et al. (2020)

et al. (2020) showed that gelatin-based coating enriched with antioxidants can reduce water loss and improve the texture of pork meat. Antimicrobial BFC has been widely studied to extend the shelf life of meat and poultry products. They are more efficient than EOs used alone (Cutter 2006). Potato starch-based films incorporated with thyme EO as an antimicrobial agent applied to chilled pork meat reduced *Escherichia coli* and *Staphylococcus aureus* growth and thus extended the shelf life by eight days longer than unpackaged meat (Yuan et al. 2021). Naseri et al. (2020) observed inhibition of the growth of total flora, coliforms, and *Staphylococcus aureus* on turkey meat wrapped with composite films based on gelatin and chitosan, incorporated with *Ferulago angulate* EO. Coating based on sodium alginate, rosemary EO and nisin was effective in reducing the growth of *Listeria monocytogenes* in poultry products during cold storage (Raeisi et al. 2016). The incorporation of antioxidant agents such as garlic or ascorbic acid in carrageenan-based coatings has been reported to improve the shelf life of poultry products (Ustunol 2009).

A comparative study on the antioxidant efficacy of different antioxidant agents (oregano and chili pepper EOs and their combination) incorporated into milk protein-based edible films for the protection of beef slices was conducted by Oussalah et al. (2004). Results showed that films incorporated with chili pepper EO were more effective than oregano in inhibiting lipid oxidation. Several other studies (Table 8.6) from different meat origins have reported the effectiveness of films and coatings in preserving the sensory and hygienic quality, as well as improving the shelf life of meat products.

8.3.4 Applications in Seafood

Due to their rich and complex composition, fish and seafood, in general, are highly perishable (Tahergorabi et al. 2015). The addition of preservatives such as phosphates is often used as a technique to increase water retention capacity, reduce oxidation and extend the shelf life of seafood products (Gram and Huss 1996). Also, freezing and deep-freezing remain the most widely used techniques to control or reduce biochemical changes in seafood products (Ghaly 2010). Biopolymers-based coatings and films have been largely used during storage to enhance the quality of seafood (Table 8.7). Several authors developed chitosan-based films and evaluated their effects on lipid oxidation during the storage of various seafood products (Jeon et al. 2002; Abdollahi et al. 2014; Gómez-Estaca et al. 2010; Günlü and Koyun 2013). The results obtained by Sathivel (2005) using chitosan and soy protein concentrate-based coating showed significant efficacy in delaying lipid oxidation for frozen salmon fillets.

Kim et al. (2012) developed an antioxidant edible film based on defatted mustard flour that was able to reduce lipid oxidation for smoked salmon without affecting the sensorial quality. A coating based on gelatin and cinnamon EO was applied to fresh rainbow trout fillets, reducing bacterial growth during 15 days of cold storage (Andevari and Rezaei 2011). *Listeria monocytogenes*, considered to be among the

Table 8.6 Recent applications of biopolymers based films and coatings on cheese

Cheese product	Biopolymers	Additives/Active agents	Application method	Storage conditions	Major findings	References
Kashar cheese	Natamycin	Oregano and rosemary essential oils	Dipping twice for 60 s and drying for 2 h	Stored at 4 °C and 70–80% RH	Inhibition of mold growth during ripening without any adverse effects on sensorial quality	Yangilar (2017)
Commercial Tybo cheese and handcraft goat cheese	Agar	Enterocins synthesized by *Enterococcus avium*	Immersion for 10 s and drying for 2 h at 30 °C and 24 h at 25 °C	Stored at 4 °C to 8 °C	Anti-*L. monocytogenes* activity, with a decrease of at least 1 log cycle in the viability of the pathogen	Guitián et al. (2019)
White brined cheese	Chitosan	Zinc oxide nanoparticle	Dipping for 1 min and drying in a laminar flow hood for 2 h at room temperature	Vacuum-packaged in plastic bags and stored at 4 or 10 °C for 28 days	Antimicrobial activity Reducing growth of f E. coli O157:H7 Preservation of color attributes	Al-Nabulsi et al. (2020)
Gouda cheese	κ-Carrageenan	Black carob extracts	Coating on both sides	Placed in the dark at 4 °C for 20 days	Antioxidant activity (reduced peroxide value)	Pérez et al. (2020)
Sliced Prato cheese	Gelatin/chitosan	Boldo extract	Covering both surfaces	Placed in Styrofoam trays, wrapped with a plastic film and stored at 4 °C for 10 days	Antioxidant and antimicrobial activity (reducing the growth of psychrotrophic and coliform counts, and reducing peroxide value)	Bonilla and Sobral (2019)

(continued)

Table 8.6 (continued)

Cheese product	Biopolymers	Additives/Active agents	Application method	Storage conditions	Major findings	References
Queso Blanco Cheese	Whey protein isolate	Oregano essential oil	Individually and completely wrapping	Stored at 8 °C with exposure to fluorescent light	Enhancing barrier properties against pro-oxidant agents Antifungal properties	Gurdian et al. (2017)
Cheddar cheese	Guargum/ Tragacanthgum		Three-laired coating by Gentle brushing approach, drying of 1 h between brushing layers and finally drying for 4 h at 24 °C	Kept at 8 °C for 90 days	Antimicrobial activity Enhancing the rate of lipolysis	Pourmolaie et al. (2018)
Goat'smilkcheese	Chitosan	Oregano and rosemary essential oils	Immersion for 30 s and drying, 2 to 3 times coating	Stored at 10 ± 5 °C, 8 ± 5% RH for 15 days	Preventing weight loss during ripening Improving microbial safety Reducing lipolytic and proteolytic activity	Embuena et al. (2017)
"Coalho" cheese	Galactomannan of *Caesalpinia pulcherrima*	*Cymbopogoncitratus* essential oil	Aseptically coating	Placed in polystyrene trays, covered with polyvinyl chloride and stored at 4 ± 1 °C	Reduction in microbial growth, especially of total coliforms Preservation of sensorial characteristics	Lima et al. (2021)

Home-made cheese	Sodium alginate	*Menthapulegium L, Artemisiaherba alba Asso, Ocimumbasilicum L, Rosmarinus officinalis L* essential oils	Immersion for 1 min, and drying at 30 °C and 60% RH for 60 min	Stored at 5–7 °C for 10 days	Prevention against weight loss, hardness, discoloration, loss off-flavor, texture, and microbial spoilage	Mahcene et al. (2020)
Roquefort cheese	Sodium alginate/ methylcellulose/ hydroxypropy methylcellulose/ sodium caseinate/ gellan gum/κ-carrageenan/ whey protein isolate / xanthan gum	Oleic acid, beeswax , potassium sorbate, Gallic Tannin and natamycin	Immersion for 1 min	Stored at 4 °C and 60% RH	Effective mass loss control during the ripening period Antifungal activity	Ordoñez et al. (2021)
Ras cheese	Chitosan/poly vinyl alcohol	Titanium dioxide nanoparticles	Brushing on the different faces of the cheese piece and drying for 2 h at room temperature	Stored at 12 ± 2 °C and about 80% RH for 3 months	Prevention of mold growth on the cheese surface during ripening	Youssef et al. (2019)

Table 8.7 Recent applications of edible films and coatings on seafood products

Seafood product	Biopolymers	Additives/Active agents	Application method	Storage conditions	Major findings	References
Salmon sushi	Furcellaran/ gelatin	Green and pu-erh tea extracts	Spraying technique (5 cm spraying distance)	Packed in sterile PET trays with a cover and stored at 4 °C for 8 days	Shelf life extension	Kulawik et al. (2019)
Fish burger rainbow trout	Chitosan	Seaweeds extracts	Aseptically coating	Were placed in trays cover with aluminum foil and stored at 4 °C	Reducing oxidation improvement in microbial spoilage control	Albertos et al. (2019)
Shrimp	Microalgalexo polysaccharides	Red seaweed extract	Dipping and draining for 5 min	Placed into open sterile Petri dishes and stored at 4 °C for 8 days	Inhibition of lipid peroxidation, protein decomposition, and bacterial proliferation Preservation of all sensory attributes	Balti et al. (2020)
Grass carp fillets	κ-Carrageenan/ gelatin/zein	Nisin/curcumin	Soaking for 30 s and airdrying at room temperature	Stored at 4 °C	Detecting the change of freshness Shelf life extension	He et al. (2020)
Rainbow trout fillets	Quinoa	Sage and lemon essential oils	Wrapping on the whole surface	Stored in refrigerator conditions for 15 days	Preventing lipid oxidation Antimicrobial activity	Alak et al. (2019)
Cold-smoked sunshine bass	Corn zein	Lemongrass essential oil/nisin	Spraying and drying for 30 min, for 2 times	Placed on sanitized plastic trays and 4 ± 1 °C	Reducing some spoilage bacteria individually (*Listeria spp.* and other Gram-positive bacteria)	Hager et al. (2019)

Bonito fish fillets	Chitosan	Peppermint essential oil	Wrapping	Packed with flexible and low-density polyethylene films and coated using pyrolytic coating devices, and stored at +4 °C for 12 days	Antimicrobial activity Shelf life extension of 6 days	Kalkan et al. (2019)
Trout fillet	Alginate coarse	*ZatariamultifloraBoiss* essential oil	Sunking for 1 min, and draining for 2 min	Stored at 4 °C for 16 days	Preservation against the growth of spoilage microflora Shelf life extension of 4 days	Khanzadi et al. (2020)
Tilapia fillets	Fish gelatin/ pectin	*Menthapulegium* essential oil	Wrapping	Stored at 4 °C for 15 days	Antimicrobial activity Preservation of physicochemical quality Shelf life extension	Aitboulahsen et al. (2020b)
Golden Pomfret	Fish gelatin	Tea polyphenol	Immersing for 30 min and drying for 60 min	Packed in high-quality polyethylene ziplock bags and stored at 4 ± 1 °C	Reducing weight loss Reducing microbial growth slowing down the myofibril degradation	Feng et al. (2017)
Boiled-dried anchovy	Fish gelatin		Coating and drying with cold-air blast for 13–15 h	Packed in a zipper film bag and stored at 20 °C	Suppression lipid oxidation (lowering oxidant factors)	Kim et al. (2017)
Sierra fish fillets	Chitosan	Tomato plant extract	Immersion for 2 min	Placed into plastic bags prior to storage-on-ice for 15 days	Shelf life extension of 5 days	Ramírez-Guerra et al. (2018)
Spanish Mackerel fish	Whey protein	Transglutaminase enzyme	Dipping for 3 min	Stored at 7 °C for 15 days	Preservation of physicochemical quality	Karina and Setiadi (2020)
Rainbow trout fish patties	Chitosan/ carboxymethyl cellulose	Glutaraldehyde and cinnamon essential oil	Separation by paper sheets	Kept in stainless steel trays at 4 ± 1 °C for 16 days	Shelf life extension antibacterial and antioxidant activity	Valizadeh et al. (2020)

bacteria of primary importance to be monitored by the seafood industry, has been retained at low levels in cold-smoked salmon coated with chitosan film containing sodium lactate and potassium sorbate (Jiang et al. 2011). Heydari et al. (2015) found a 1.5 $\log_{10}$ CFU/g reduction in the microbial population in carp fillets packed with sodium alginate films with mint EO. This film resulted in a considerable reduction in total volatile basic nitrogen (TVBN) levels during the storage of the wrapped fillets compared to the control fillets. In another study, Gómez-Estaca et al. (2010) evaluated the antimicrobial effect of different composite films based on gelatin and chitosan incorporated with eight EOs (clove, fennel, cypress, lavender, thyme, verbena, pine, and rosemary) against six types of bacteria responsible for fish spoilage. The results showed that the films incorporated with the clove EO had the best antimicrobial activity and therefore was applied on fish fillets and monitored during storage. The authors found that composite films containing this EO allow a controlled release of the active substances of EO and maintain a sufficient concentration over a longer period, and therefore a considerable reduction in bacterial growth during the storage of fish fillets.

8.4 Limits of Application

Edible films and coatings are among the most promising preservation methods for foodstuffs. Their main drawback, however, is their specificity. For instance, for fresh or freshly cut fruits and vegetables, coatings should be optimized for each species and each cultivar (Porta 2013). Therefore, to obtain the desired results, the biopolymer type, concentration, and/or the coating formulation must be well controlled. Besides, storage conditions could influence the behavior of packaged or coated foods. Thick films or coatings could cause anaerobic conditions that could lead to undesirable flavors. Films and coatings with high WVP result in weight loss and therefore, loss of appearance and texture of the product. Conversely, films and coatings with low gas permeability will prevent the transfer of the amount of oxygen required for the fruit's ripening phase. Also, the risks of microbial proliferation often increase, depending on the relative humidity of the environment, as well as the solubility of BFC, which can dissolve during storage and promote microbial proliferation (Menezes n.d.). On the other hand, food application methods for BFC must be enhanced and adapted to industrial-scale applications and ensure homogeneous and uniform application on the product surface with effective drying (Lin and Zhao 2007).

Several authors have focused on the constraints and limits encountered when applying an edible and bioactive film or coating as a food packaging. Hager et al. (2019) reported that nisin is not commonly used as an active agent in the formulation of bioactive films, despite its proven antimicrobial effects, due to its high cost. Also, the production and marketing of such bioactive film-coated products worldwide are limited, due to the variety of regulations and standards that differ between countries. Sensorial quality could also limit their application in foods in particular, for films and coatings incorporated with EO_S. In this sense, Cano Embuena et al. (2017) applied one, two, and three layers of coating incorporated with EOs for goat cheese preservation and found that the cheese coated with a triple layer coating received the lowest sensory scores, because the smell, flavor, and taste of cheese were affected by the EOs.

8.5 Conclusions

The research and studies conducted on BFC have been highlighted in this chapter. Edible films and coatings could be an important alternative method toward replacing the unnecessary use of plastic-based, hazardous, and non-biodegradable synthetic packaging. The various functions of BFC based on their potential applications for food preservation were also explained. Composite films combining the use of several biopolymers in the matrix of BFC offer numerous advantages, such as the possibility of taking advantage of the different properties of each compound to obtain a film or coating with the desired qualities. Moreover, the incorporation of antimicrobial agents like EOs is an efficient way of enhancing the hygienic quality of food products. Efforts should be made to resolve, on the one hand, the challenges of industrial development and marketing and, on the other, the regulatory constraints of implementation, which differ between countries.

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Role of Sensors to Improve Food/Beverage Packaging

9

Mariusz Tichoniuk

Abstract

Traditionally, food and beverage packaging focus on the protection of its content and information on them within the supply chain. The development of modern packaging materials and technologies provides an opportunity to improve the communication on the product state and its surrounding. Sensors dedicated to food and/or beverage packaging could be simple time-temperature indicators or chemosensors sensitive to food spoilage products. A gas indicator implemented in the packaging could reveal its leakage or the development of undesirable processes in the packaged product. A wide variety of electrochemical sensors (e.g. temperature or humidity sensors) can work independently or are combined with advanced data carriers such as radio-frequency identification (RFID) tags. The application of sensors in various parts of the food/beverage supply chain could improve its controllability and reduce the scale of food waste more efficiently. The consumer will also appreciate a simple indicator informing about the freshness of food or the correct temperature of the drink.

Keywords

Food/beverages packaging · Sensors · Smart packaging · Intelligent packaging · Indicators · Data carriers

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9.1 Introduction

Food and beverages are a very diverse group of products that provide consumers with the required nutrient compounds, biologically active components in the diet, but also the pleasure of consuming our favourite dishes. Current trends in food and beverage consumption are in the strong influence of customer expectation for convenient, ready to eat and/or low processed products with unchangeable quality and extended shelf-life (Han et al. 2018; Rai et al. 2019). Most food products are a complex mixture of ingredients that are sensitive to external physicochemical factors, microbial contamination and biochemical processes occurring in the products themselves, and require protection against factors that could lower their quality and affect safety (Fuertes et al. 2016; Sohail et al. 2018; Witjaksono et al. 2018). Food, by definition, must be safe, but consumers demand also information about its composition, use-by date, method of preparation, and many other data associated with food storage and consumption. Traditionally, the need for food packaging stems from its practical applications of holding goods together and protecting them within the supply chain until the food or beverages reaches the end-user (Lydekaityte and Tambo 2019). According to FAO reports, about 14% of food products are lost in the food supply chain before they reach the final consumer (FAO 2019). In addition to the protective function, the packaging in its original use is intended to facilitate handling the packed product in storage and transportation and to communicate about the properties of their content (Vanderroost et al. 2014; Müller and Schmid 2019). The protection against adverse physical conditions, chemical and/or microbial contamination is an obvious result of the barrier capabilities of packaging construction and materials, which is a passive, conventional way of the product preservation against external factors occurring in the supply chain (Schaefer and Cheung 2018; Drago et al. 2020). The information contained on packaging provides important knowledge about the origin of the product, its weight/volume, ingredients, nutritional value, expiration date, precautions for use as well as the conditions of transport, storage and utilization, if necessary (Fuertes et al. 2016). Packaging should improve the convenience of food product consumption and distribution by the adaptation to customer's lifestyle and physiological capabilities (e.g. by the selected package size and easier food preparation) and to transportation/storage technologies (e.g. using standard packaging shape and dimensions, introduction of useful holders and fixings) (Müller and Schmid 2019). The same is referred as to the containment of food products which should ensure ease of their transportation and handling in the supply chain and the right portion of products for the final consumers (Schaefer and Cheung 2018).

The development of innovative materials and packaging technologies enabled the extension of the information functionality of conventional packaging by the introduction of intelligent systems (Mustafa and Andreescu 2018). The intelligent packaging for food products is recognized as material and article that monitor the condition of packaged food or the environment surrounding it (Commision Regulation 2009 (EC) No 450/2009). The intelligent food packaging systems are designed to monitor and signalize the changes of packed products and its surrounding in the

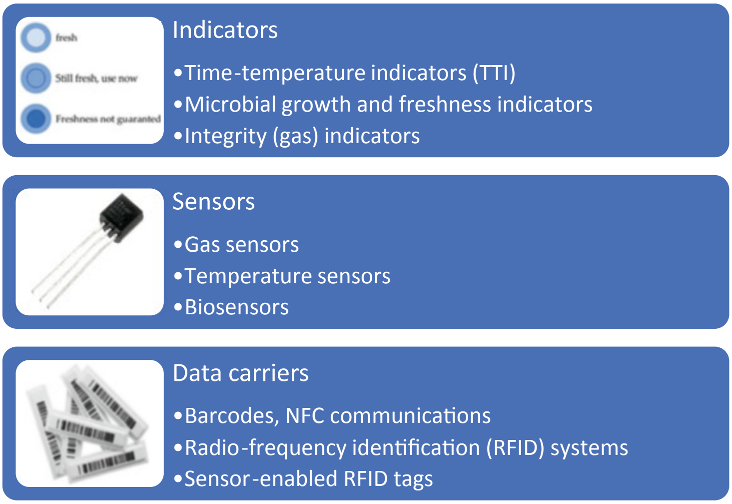


Fig. 9.1 General types of intelligent packaging systems applied for food and beverages packaging (Source: Own work based on Ghaani et al. 2016, Sohail et al. 2018, Tichoniuk 2019, Drago et al. 2020)

food supply chain, which can facilitate decision-making procedures focused on preserving food quality, and indirectly extend its shelf life and/or improve overall safety (Müller and Schmid 2019). The subject of the real-time monitoring can be internal and external characteristics of the packaging environment (e.g. temperature, humidity), food freshness or microbiological condition, the integrity of packaging or location of the packaged product (Sohail et al. 2018; Chowdhury and Morey 2019). The functionality of intelligent packaging is based on the recognizing element that interacts physically and/or chemically with the monitored environment or product and signalizes the change of observed phenomena. This mechanism relies usually on the application of one of the specific sensors, indicators, or other data transmission items, that enables the collection and/or transfer of information through the packaging (Fig. 9.1). The upgrade of conventional packaging to the intelligent one often relies on attaching an external recognition element (for the product surrounding monitoring or data transmission) or internal sensor or indicator (for monitoring of packed product condition) (Fang et al. 2017; Mustafa and Andreescu 2018). A more detailed classification of intelligent packaging solutions is presented in Fig. 9.1, but it should be remembered that this is not an absolute distinction of types and they may be classified differently according to various sources. This applies in particular to the distinction between indicators and sensors, which both recognize the target compounds or physical phenomena, and the assignment to one or the other category is more related to the interpretation of the results provided.

Sensors and indicators are constructed to provide information relating to the product quality connected with the temperature measurements (time-temperature indicator, temperature sensor) or the presence of specific chemical compounds (gas sensor/indicator, microbial growth or freshness indicators, biosensors) (Ghaani et al. 2016; Sohail et al. 2018; Tichoniuk 2019). Data carriers implemented in intelligent packaging (barcodes, NFC communication, radio-frequency identification systems) are designed to support the management of supply chain logistics (Tichoniuk 2019; Drago et al. 2020) (Fig. 9.1). More reliable and effective communication can also serve to significant improvement of product traceability in the supply chain. A combination of RFID systems with sensors, that monitor the condition of products and their surroundings, could influence the reduction of food waste during food storage and distribution (Ghaani et al. 2016). Intelligent packaging with the function of data transfer might be implemented in Automatic Data Collection (ADC) system and support IT solutions such as Warehouse (Logistic) Management System (Yu et al. 2020).

Sensors, indicators and/or data carriers implemented in intelligent packaging support many aspects of food product preparation and distribution in the supply chain. The real-time information about the packed food or beverages and its surrounding is used to monitor and adjust the conditions within the supply chain and to make decisions affording the extension of food shelf-life, improve safety, ensure quality, provide information and warn against the threat for the final consumer (Drago et al. 2020). Besides the identification of target compounds or physical phenomena, intelligent packaging has the potential to support the effectiveness of different parts of the supply chain and reduce food waste (Yu et al. 2020).

According to the Deloitte report on the market potential of smart packaging, the innovative packaging systems could be successfully applied in three main areas (Deloitte 2018):

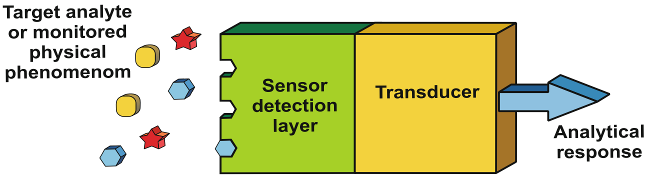
1. Inventory and product life cycle management
2. Product integrity assessment
3. Supporting consumer experience

Intelligent packaging with gas sensor, food freshness indicator or adopted for this purpose time-temperature indicator can be used by each member of food supply chain to the estimation of real end-of-life point for food and beverage considering the actual conditions within the distribution chain (regardless of the initially specified product expiration date) (Müller and Schmid 2019). A widespread introduction of intelligent systems for the supply chain would make it possible to change so-called fixed shelf life (FSL) estimation for food and beverages product into dynamic shelf life (DSL) attitude. The adjustable product expiration date (with DSL approach) could reduce food waste as consumers will be able to check the actual condition of food/beverages and their suitability to consumption (Herbon et al. 2012; Albrecht et al. 2019).

9.2 Sensors: Types and Construction Principles

The development of intelligent food and beverage packaging is strictly associated with the incorporation of sensors or indicators into its construction, which enables the assessment of packed product quality or the condition of its surrounding (Kuswandi and Moradi 2019). The sensor interacts with an internal target (e.g. food component, volatile metabolite in the packaging headspace) and/or external factor (e.g. temperature, a component of the atmosphere) (Realini and Marcos 2014). The main challenge in the sensor construction is to establish a reliable relationship between the result of the interaction and information about the state of the packed product and/or its surrounding (Fuertes et al. 2016; Poyatos-Racionero et al. 2018).

From the technical point of view, the sensor consists of two basic elements (Fig. 9.2)—chemical or biological receptor, that reacts specifically with the target analyte, and a transducer converting the analytical response into a recognizable signal, which can provide quantitative and/or qualitative output of the sensor activity (Nayak et al. 2009; Mustafa and Andreescu 2018). Biosensing systems rely on the recognition systems of biomolecules like enzymes, nucleic acids, immune system components (antigen, antibodies) or other bioactive compounds (Wang et al. 2012; Chauhan et al. 2019). The sensor transducer can be based on many different physicochemical and electronic solutions, which convert the observed target reaction into a useful analytical signal. Depending on the nature of this reaction, the transducer may use colorimetric arrays (Yang et al. 2011), electrochemical (Pwavodi et al. 2021), optical (Viter et al. 2017) or mass-based signal transmission (Debabhuti et al. 2021). Biosensors are usually designed for use in medical research or environmental protection, but the newest intelligent packaging is slowly starting to adopt these analytical devices (Mustafa and Andreescu 2018). Biosensing devices are



Types of receptors:
1. **Chemical**
2. **Electromagnetic**
3. **Mechanic**
4. **Optical**
5. **Thermal**
6. **Acoustic**
7. **Biologically active (biosensors)**

Types of transducers:
1. **Electrochemical**
   (*e.g.* conductometric, potentiometric)
2. **Optical**
   (*e.g.* Surface Plasmon Responce, UV-Vis absorbance)
3. **Thermal**
   (*e.g.* heat sensitive change in polymer film)
4. **Mass-based**
   (*e.g.* piezoelectric, magnetoelastic)

Fig. 9.2 Types of receptors and transducers in sensors construction (Source: Own work based on Sohail et al. 2018, Chauhan et al. 2019) commonly developed in laboratories, and their creators' aim is to achieve popularity at least equal to biosensors used to monitor blood glucose levels (glucometers currently account for 85% of commonly available biosensors) (Pereda et al. 2017).

A more direct assessment of the condition of the packed food or beverages is provided by the indicators, which signalize any change in packed product or its surrounding (e.g. pH, temperature) usually by visual changes (e.g. by changing the colour) (Sohail et al. 2018). The indicators have usually simplified recognition and transduction system in comparison to the sensors. Indicators provide direct and noticeable to the naked eye change the appearance of the their distinctive elements in the presence of the target phenomenon. The greatest challenge in the design of a usable intelligent packaging system is the identification of a reliable relationship between the measurable indicator and changes in food product quality and/or safety being under observation (Müller and Schmid 2019). The most popular indicators applied in intelligent food packaging are time-temperature indicators (TTI) mainly because of the simplicity of its construction, low cost, ease of calibration and interpretation of results compared to other indicators and sensors (Han et al. 2018). Packaging tightness indicators (gas indicators) and food freshness indicators (including ripening indicators and microbial growth indicators) are also becoming more and more popular (Drago et al. 2020).

9.3 Physical Sensors/Indicators

Temperature is one of the most important physical agents affecting the condition of food and beverages (especially refrigerated products and frozen food) (Fuertes et al. 2016). Deviations from the determined temperature profile lead to noticeable food changes or significantly increase the likelihood of these changes, which should be recognized in prerequisite kinetic study and modelling of food quality loss at different temperature levels (Kim et al. 2016). The simplest physical sensors applied in food and beverage packaging are designed for temperature monitoring base on the application of thermochromic inks which can change their colour as a result of exposure to elevated temperature. The colour changes can be reversible or irreversible depending on the thermochromic ink applied. Irreversible changes remain stable when the packed product reaches the specified temperature and the packaging element does not revert to its previous appearance until excessive cooling or overheating subsides (Vanderroost et al. 2014). The intelligent packaging can indicate undesirable exposure of the packed product to too high or too low temperature, which can be a desirable application of the indicator in the food supply chain. The reversible thermochromic inks systems are more desirable by the final food or beverages consumers. The temperature colour-changing imprints on the packaging may indicate the desired temperature of consumption of a given product (e.g. a chilled drink—Fig. 9.3a) or remind about the necessity to refrigerate a product that is sensitive to prolonged exposure to elevated temperatures (Fig. 9.3b).

The monitoring of thermal conditions of food storage and/or transportation can be easily carried out with time-temperature indicators (TTI) (Fig. 9.4) which are the

Fig. 9.3 Examples of food and beverages packaging imprinted with thermochromic ink indicating (**a**) optimal cooling temperature or (**b**) a warning of increased temperature of the packed product (Source: Image provided by Chromatic Technologies Inc.)

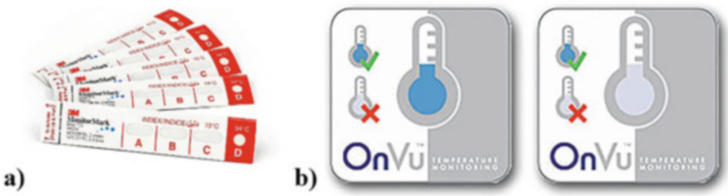


Fig. 9.4 Examples of commercially available time-temperature indicators: (**a**) Monitor Mark™. (**b**) OnVu™ labels (Source: Images provided by 3M Company (**a**) and Freshpoint (**b**))

most popular intelligent packaging items (Müller and Schmid 2019). TTI indicators activity relies on different types of reactions, the intensity of which is proportional to the temperature increase above the assumed optimal value. The mechanisms can have mechanical (e.g. 3M Monitor Mark™), chemical (e.g. On Vu™, Fresh Check®), electrochemical (e.g. VITSLAB®), enzymatic (e.g. CheckPoint®) or microbiological (e.g. e0®, TopCryo®) background but the main goal is to provide irreversible and visible reaction of TTI indicator dependent on the monitored temperature of the packed product or its environment (Pereira Jr. et al. 2015; Wang et al. 2015). Table 9.1 presents commercially available TTI indicators and a short description of its operation modes.

Time-temperature indicators are designed to have a convenient and simple form of an element that can be easily inserted into conventional food packaging such as labels or strips. TTI indicators work usually in one of three modes: indicating the transgression of determining temperature (critical temperature indicators), measuring the time of exceeding the indicated temperature (partial history indicators), or recording the complete temperature profile in a given period (full history indicator) (Müller and Schmid 2019). The indicator should respond when the adverse thermal

Table 9.1 Commercially available time-temperature indicators applicable for food and beverages intelligent packaging

TTI indicator (company, country)	Type of action	Need of activation	Colour change (optical response)	Application
CheckPoint® types M, L (Vitsab Int. AB, Sweden)	Enzymatic	Yes	Tricolour: green to yellow to red	Meat, fish, dairy products
(e0)® (Cryolog, France)	Microbial	No	Green to red	Cold chain
FreshCheck® (TEMPTIME Corp. USA)	Polymeric	No	Colourless to blue	All kinds of fresh products
On Vu™ (Freshpoint, Switzerland)	Photochromic	Yes	Dark blue to colourless	Meat, fish, dairy products
Monitor Mark™ and Freeze Watch (3M Comp. USA)	Diffusion-reaction	Yes	Diffusion of coloured path/ material	Bakery products, beverage, meat

Own work on the basis (Park et al. 2015; Sohail et al. 2018; Drago et al. 2020)

Fig. 9.5 CheckPoint® label L5-8 (Smart TTI Seafood Label) indicating thermal exposure over the level recommended by U.S. Food and Drug Administration (Source: Image provided by Vitsab International)

condition occurs and provide information about the scale of the risk of food quality and safety loss (Fig. 9.5).

The usefulness of colorimetric indicators for all members of the food supply chain depends on the technological applicability of the indicator on the packaging and the readability of its signalling (especially for the final consumer) (Schaefer and Cheung 2018). A very good example to consider these two aspects of TTI application on food packaging is On Vu™ time-temperature indicator that can be activated by UV radiation at any stage of the supply chain. On the other hand, its response to the adverse thermal condition is fading the dark navy blue interior of the pictogram to grey colouring, which gives only the approximate time of unfavourable temperature influence on the monitored product (Branka 2012). The thermochromic inks used in physical sensors for intelligent packaging should provide a more distinguishable change of the indicator appearance, which will be easy to recognize in a situation threatening food safety and quality.

9.4 Chemical Sensors/Indicators

The atmosphere inside packaging has a tremendous influence on the quality of packed food and/or beverages, and some changes in its chemical composition indicate often undesirable processes in packed product or leakage from inside or outside of the packaging materials (Sohail et al. 2018). The chemical sensors are constructed to detect target analytes in the packaging atmosphere or close contact with packed food products (Table 9.2). This mechanism of action is exploited by integrity and food freshness indicators/sensors (Fuertes et al. 2016). The first type of intelligent packaging is based mainly on oxygen or carbon dioxide detection. When it is applied as an integrity indicator, it contains a dye compound that changes its colour in case of alternation of the chemical composition inside packaging (Meng et al. 2014).

The integrity (gas) sensor or indicator is very usable for food packaging with the modified atmosphere inside, when the chemical content of packaged product headspace prolongs its shelf life, and damage to the integrity of the packaging reduces the effectiveness of the applied packaging system. One of the most popular integrity indicators that is available on the market is Ageless Eye® label (provided by Mitsubishi Gas Chemical company) (Fig. 9.6). The indicator enables the detection of an oxygen level increase inside the packaging but it should be implemented together with oxygen scavengers to prevent the influence on the reliability of the indicator by residual oxygen, which could be present in the packaging or could be released from the packaged product (Tichoniuk 2019).

The release of metabolites from packed food could indicate a significant decrease in its quality and/or safety due to the development of undesirable microflora or as a result of internal physicochemical and/or enzymatic changes in the product. Freshness indicators and sensors are designed to recognize metabolites released into the packaging interior during food spoilage or ripening (Fig. 9.7). The target analytes in the recognition process are usually carbon dioxide, ethyl alcohol, esters, organic acids, sulphur derivatives or volatile nitrogen compounds (Sohail et al. 2018; Tichoniuk 2019). The freshness indicators are usually simple colorimetric arrays

Table 9.2 Examples of target compounds and food products monitored by freshness indicators

Target compounds (metabolites)	Food product	Freshness indicator/sensor
Biogenic amines	Fish, seafood, meat	Colour-changing indicator with pH-sensitive dye/electrochemical sensor for enzyme redox reaction
Carbon dioxide	Fermented food, meat	pH-sensitive with colorimetric response/electrochemical sensor, e.g. with silicon-based polymer recognition layer
Glucose/ Lactic acid	Fermented food, meat	pH-sensitive with colorimetric response/electrochemical sensor for redox reaction
Oxygen	Meat, fruits, vegetables	Oxygen-sensitive indicator with pH-sensitive dye/optical sensor by fluorescence

Own work on the basis of Sohail et al. (2018)

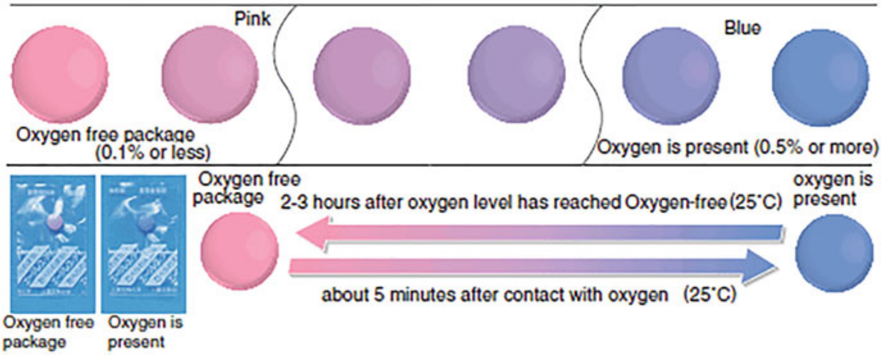


Fig. 9.6 Ageless Eye® gas (oxygen) indicator (Source: Image provided by MITSUBISHI GAS CHEMICAL)

Fig. 9.7 RipeSense fruits ripening indicator (Source: Image provided by Ripesense Limited)

that change their colour in the presence of target chemical compounds and signal change of product quality or loss of freshness (Fuertes et al. 2016).

The intelligent packaging systems able to monitor food freshness and/or ripeness are intensively developed but some of them are already available on the market (Table 9.3). Most of the published research results focused on the application of freshness indicator for non-destructive monitoring of food spoilage metabolites in the packaging headspace during the storage of packaged perishable foods

Table 9.3 Examples of commercially available chemical indicators applicable in food and beverages intelligent packaging

Type of indicator	Commercial name	Company (Country)	Area of application
Integrity (gas) indicator	Ageless Eye®	Mitsubishi Gas Chemical (Japan)	All packed food products—specially applicable in aseptic and modified atmosphere packaging systems
Integrity (gas) indicator	Novas®	Insignia Technologies (United Kingdom)	
Freshness indicator	Fresh Tag®	COX Technologies (USA)	Perishable food products, with volatile metabolic products, e.g. meat, fish and seafood, dairy products, vegetables and fruits
Freshness indicator	Raflatac	VTT and UPM Raflatac (Finland)	
Freshness indicator	RipeSense	RipeSense (New Zealand)	
Freshness indicator	SensorQ®	DSM NV and Food Quality Sensor International Inc. (Denmark)	

Source: own work based on (Fuertes et al. 2016; Ahmed et al. 2018; Poyatos-Racionero et al. 2018)

(e.g. vegetables, fruits, seafood or meat) (Ahmed et al. 2018; Tichoniuk et al. 2021). The colorimetric freshness indicators are very promising elements of intelligent packaging, but their effectiveness and credibility of the information provided depend on many factors such as positioning inside the package, indicator's activation procedure, the chemical content of packaging atmosphere, or temperature changes within the whole food supply chain (Tichoniuk et al. 2017). The influence of the above-mentioned factors has to be considered both in the laboratory study on new freshness indicators and in the evaluation of commercially available indicators. Table 9.3 presents the indicators dedicated to food freshness and tightness of their packaging that are available on the market and are recognizable elements of intelligent packaging. Freshness indicators could be a very good tool for the introduction of dynamically adjustable expiration dates in the so-called dynamic shelf life (DSL) approach in the food supply chain. However, due to technological limitations, they give way to TTI indicators, which can be much easier implemented on a mass scale in intelligent packaging (Herbon et al. 2012; Albrecht et al. 2019). The application of time-temperature indicators in the food supply chain based on DSL attitude can reduce food waste by retailers and help to maintain food quality and safety for the final consumers (Buisman et al. 2019).

9.5 Electronic Sensors and Data Carriers

Food and beverages distributors appreciate the ability to trace their products along the supply chain thanks to intelligent packaging designed for efficient data transfer. Data carriers are not designed to monitor the condition of a packed product (or its surrounding), but they are intended to facilitate the flow of information in the supply chain (Müller and Schmid 2019). This group of packaging systems includes different variations of barcodes one-dimensional and two-dimensional (e.g. Quick Response (QR) codes), radio-frequency identification (RFID) systems, and their combinations with sensors such as temperature or mechanical shock sensor (Fang et al. 2017; Yu et al. 2020). Barcodes are now the global standard for capturing and communicating product information throughout the supply chain (GS1 2020). A typical one-dimensional barcode consists of a set of black and white bars and a corresponding numeric notation of encoded information. Two-dimensional (2D) barcodes have a square or rectangular shape and contain black and white spots creating the whole pattern and encoding required information. All these codes are printed on the surface of the packages and are used in optical Automatic Data Collection (ADC) systems, but intelligent packaging technology enables data transfer without visual contact with the label using electromagnetic waves in RFID technology (Yu et al. 2020).

Radio-frequency identification (RFID) systems are emerging intelligent packaging technology usable in real-time data collecting, storage and transmission, which do not require direct contact and visibility of carriers (labels or tags) (Poyatos-Racionero et al. 2018). RFID systems exploit electromagnetic fields to collect and transfer information about the packed product for its automated identification and traceability (Abad et al. 2009; Yu et al. 2020). Radio-frequency tags can be divided into three main groups depending on applied power supply, the ability of communication and implementation of additional features (e.g. temperature measurement). The most advanced are active RFID systems, less developed are semi-passive or semi-active labels, and the simplest construction have passive RFID tags (Poyatos-Racionero et al. 2018). The radio-frequency identification tags contain an integrated electronic circuit built into an antenna for the transmission of data stored in the chip to a reader, which enables a different type of packaging to be monitored at the same time and collect various information. The tag can be coupled to a primary food packaging, box, transportation container, or pallet and therefore can be identified and tracked (Cerqueira et al. 2018; Sohail et al. 2018). Table 9.4 presents examples of commercially available RFID systems combined with sensing arrays designed for food packaging. Such sensors could be used to monitor the freshness and current state of perishable food products in the supply chain to minimize the risk of delivering spoiled food to the final consumer.

A market simulation performed for the inventory management of perishable food products in a dynamic pricing system and with the application of RFID tags with TTI indicators confirmed the usability and economic justification of the application of such intelligent packaging in the supply chain (Herbon et al. 2012). According to the researches the introduction of RFID systems combined with the time-temperature

Table 9.4 Examples of commercially available RFID systems combined with sensors for food packaging

Commercial name	Company	RFID system
Easy2log®	CAEN RFID Srl	Time-temperature sensor tag
CS8304	Convergence Systems Ltd.	Time-temperature sensor tag
TempTRIP	TempTRIP LLC	Time-temperature sensor tag
Intelligentbox	MondiPlc	Box with integrated time-temperature sensor tag
Intelligentfishbox	CraemerGroup GmbH	Box with integrated time-temperature sensor tag

Source: own work based on (Fuertes et al. 2016; Poyatos-Racionero et al. 2018)

sensor is profitable (at all price discrimination levels) provided the penalties for the sale of damaged items are high and the cost of using intelligent packaging is relatively low. On the other hand, the increase of packaging cost by over 30% of the value of a packaged item and relatively low penalties for selling bad quality products may make the introduction of intelligent packaging unprofitable. However, in the market where customers' awareness of product quality is strong, using TTI-RFID automatic devices can be very profitable in connection with pricing differentiation. Radio-frequency identification systems were also introduced into food quality and safety assurance approaches, for example, for food cold chain monitoring (Badia-Melis et al. 2015), food freshness (Eom et al. 2014), or food product stored in modified atmosphere packaging (Martínez-Olmos et al. 2013).

The most desirable intelligent packaging for food and beverages, considered by both consumer and supplier, includes sensors and indicators used to expand its informative functionality of packaging (Schaefer and Cheung 2018). Figure 9.8 presents QLIKTAG project of food packaging featured with barcodes, Quick Response (QR) codes, and authentication tags to provide all participants of the supply chain additional information about the product. Additionally, Internet of Thing (IOT) technologies could be also connected with intelligent packaging in the food supply chain to support product traceability, monitoring food products' condition, and live-sharing the collected data with the chain participants. (Witjaksono et al. 2018). All mentioned smart technologies could include simple indicators or sensors such as temperature or integrity ones especially usable for monitoring product quality and safety (Fuertes et al. 2016).

9.6 Summary

Real-time control of food and beverages condition and evaluation of its surrounding could be facilitated with intelligent packaging systems. Indicators and/or sensors, included in this packaging group, are capable of real-time monitoring selected parameters influencing the quality and safety of food products such as temperature

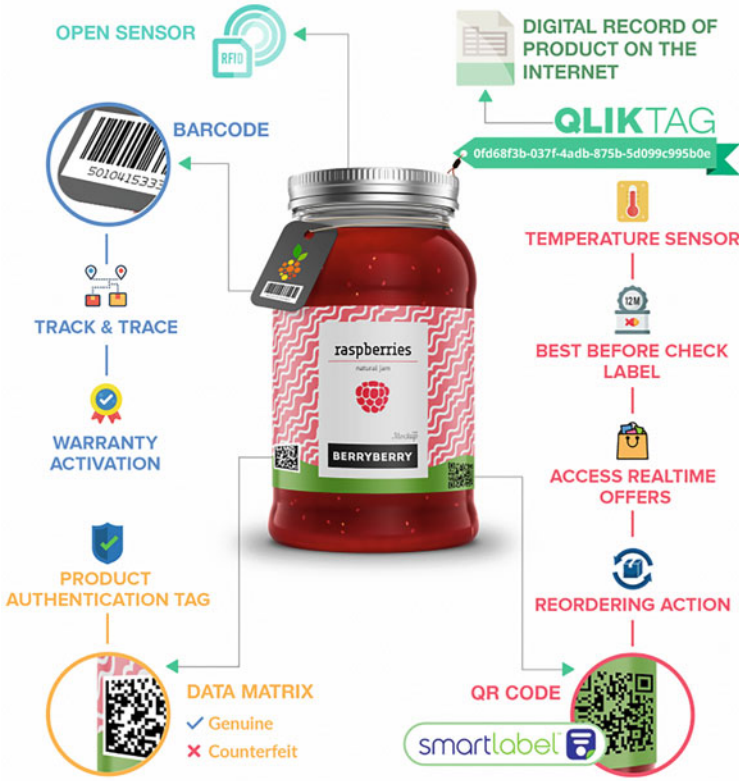


Fig. 9.8 Example of intelligent (smart) packaging designed for food products and equipped with different identification tags and data carrier labels (Source: Image provided by Qliktag Software Inc.)

or chemical composition of the atmosphere inside the packaging. They could be also adjusted to recognize symptoms of food ripening or spoilage, e.g. detecting pH change or confirming the presence of volatile metabolites being the results of undesirable changes in food and beverages quality. However, intelligent packaging systems require validation of its signalling about the changes in monitored product or its surrounding regarding the influence of external factors on the indicator/sensor activity.

The electronic data carriers based on Radio Frequency Identification (RFID) technologies are already introduced in many areas of the supply chain, which supports the flow of information during product storage and distribution. RFID systems could facilitate real-time product monitoring, more efficient inventory and precise product traceability, which support the maintenance of food product quality and safety. RFID tags combined with electronic sensors such as temperature recorders or gas sensors could be very useful in the supply chain, especially for perishable food products. Additionally, Internet of Thing (IOT) elements introduced into intelligent packaging in a form of QR codes or product authentication tags, for example, significantly extends the possibility of obtaining additional information about food products for all members of the food supply chain (and especially for the final consumers).

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Functional Nanomaterials for Food Packaging Applications

10

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Abstract

The utilization of nanotechnology in the establishment of innovative food packaging materials has had a significantly remarkable enhancement in the previous years, and researches are expected to have an essential impact on the food packaging market in the coming years. Nanotechnology is the emerging engineering field of functional system at the molecular level and has the potential to play a significant role in agriculture and food security, molecular and cellular biology sensors for pathogen identification, environmental protection and allows designers to change the packaging materials on the molecular level to enhance their desired properties such as mechanical strength, temperature and moisture stability, long durability, gas barrier, and flexibility. Due to the revolution in the food packaging materials, the traditional packaging is being replaced by the active packaging, biochemical improved packaging, physically improved and smart packaging to enhance food quality and safety with the significant use of nanotechnology. The focused application of nanotechnology is utilized in food packaging because of their better balance in processing, characteristics, and overall production cost. Nowadays the country regulations and the market are claiming for sustainable higher performance of the food packages, such as longer shelf life, maximum ways of preserving the food in better conditions and shows lower environmental impact. The most promising approaches to overcome defined problems with success have been significantly achieved by preparing nanotechnology-based food packaging material, for instance, preparing nanocomposites that are based on inorganic nanoparticles and polymer matrix dispersed as reinforcement. The techniques used with high aspect ratio of nanoparticles allow adding new functionalities to traditional packaging materials,

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for example, antimicrobial activity, control emitter substances, and enhanced gas and water vapor barrier characteristics. The main classification of nanotechnology packaging materials and their significant functions and applications are reviewed in this chapter with safety concerns and future prospective.

10.1 Introduction

The major losses in the food industry are wastage of more than 1.3 billion metric tons of consumable food every year. The more focused reason behind the loss is low-quality post-harvesting techniques, unsuitable storage facilities, transport facilities, and also last but not the least wastage of food in the marketplaces as well as by consumer uses (Reynolds 2007). The food production rate is increasing on one side but on the other side to focus on solving the problem of food crises due to food wastage, environmental adverse conditions as well as increase in greater population rate. Researchers and scientifically proven studies showed that food wastage is mostly born due to microbial contamination; this will lead toward deterioration in shelf life of food products and also increases the high risk of foodborne diseases (Sperber 2009). The problem of food commodities storages and decrease in shelf life of food products were minimized by the use of "nano-packaging for food" or utilization of nanotechnology (Ekrami et al. 2014). Nanotechnology is the combination of development, fabrication, and characterization of material or the structure measures length in the nanometers. If a macro-sized particle lowers down to a nano-size particle, the producing nanoparticles have entirely different chemical and physical property from the original macro-size particles (Ravichandran 2009). Nanoparticles are the owner of unique characteristics of physical, chemical, biological, and large surface area volume ratio. This newborn technology helps in improving better health, quality of life, wealth as well as also shows significantly positive impact on the environmental issues (Dasgupta et al. 2015). Besides the tremendous development of nanomaterial in the field of agro-food, sewage treatment, medicines, and electronics, it lacks behind in the field of food packaging. However, since various nanomaterials developed with many functional properties can be used to improve the quality of food packaging, hence even in its infancy, the nonomaterials are being developed and applied increasingly in the food packaging industry nowadays (Kuswandi 2017).

The utilization of functional nanomaterials for food packaging could also be helpful in developing properties which could modulate the release of antimicrobials, antioxidants, enzymes as well as flavors nutraceuticals to enhance the shelf life and overall quality of food (Berekaa 2015). Nanotechnology helps in manufacturing nanomaterials in a form of film which works by refusing permeability of unwanted gases such as carbon dioxide or oxygen, which affect the shelf life of food products (Silvestre et al. 2011). Previously plastic polymers of non-biodegradable nature were mostly used for food packaging but these are a threat to human beings, animals, and the environment too. The biomaterials are edible and biodegradable in nature and can be used in food packaging to maintain food product freshness and food safety during distribution, storages, and consumption period. Nanotechnology used for food packaging is based on nanocomposite material to reduce the wastes of the food packaging (Kuswandi 2017). The nanocomposite materials are helpful in biodegradation film, edible, environment friendly, easy to coating, and significantly manage freshness and shelf life of food (Sorrentino et al. 2007).

The nanotechnology sector emerges very fast but in nano-food packaging it is still playing a role of infancy. The present chapter focuses on acknowledging the recent methodologies in the development of nano-food packaging. Covered topics include the functional nanomaterials used for the improvement of food packaging and classification, physical improved packaging consists of nano coatings, nano surface biocides, nano-laminates for enhancing physical, mechanical, barrier, and stability, biochemical improved packaging consists of various bio-based nanomaterials for enhancing biodegradability and eco-friendly, improved packaging with active functions such as UV absorbing film, scavenger film to protect from oxygen, antimicrobials, improved packaging with smart functions such as nanosensors for freshness identification, oxygen detection, techniques to analyze functional nanomaterials, environmental and safety concerns and the chapter ended with future prospective and conclusion.

10.2 Classification of Nanomaterials-Based Food Packaging

The utilization of nanomaterials in food packaging is divided into two main classes: firstly, nano-object materials and second one is nanostructured materials. The application of nano-object materials is as fillers in the nano-plates and nanofibers, for example: carbon nanotubes, metallic nanoparticles. In the case of nanostructured material, the nanomaterials are utilized into matrix of polymer by the dispersion of nanostructured materials in the form of nanocomposites as shown in Fig. 10.1.

Food packaging can be improved by incorporation of nanomaterials and they can be categorized into four main classes on the basis of the functions of nanomaterials (Table 10.1). Physically improved packaging; the nanomaterials improve the physical properties of packaging such as temperature and moisture stability, mechanical strength, durability and gas barrier and flexibility properties. Biochemical improved packaging; the biochemical characteristics of packaging such as biodegradability, eco-friendly, edible and low waste generation. Improvement of packaging by active functions of nanomaterials as antimicrobial properties also includes antioxidant and UV absorbance. These properties were intentionally introduced into and show a positive effect on the packed food regarding taste, freshness, and shelf life. Smart functions of nanomaterials are used to improve food packaging by utilization of nanosensors to examine and monitor the condition of the food in terms of freshness, oxygen and pathogen level, etc.

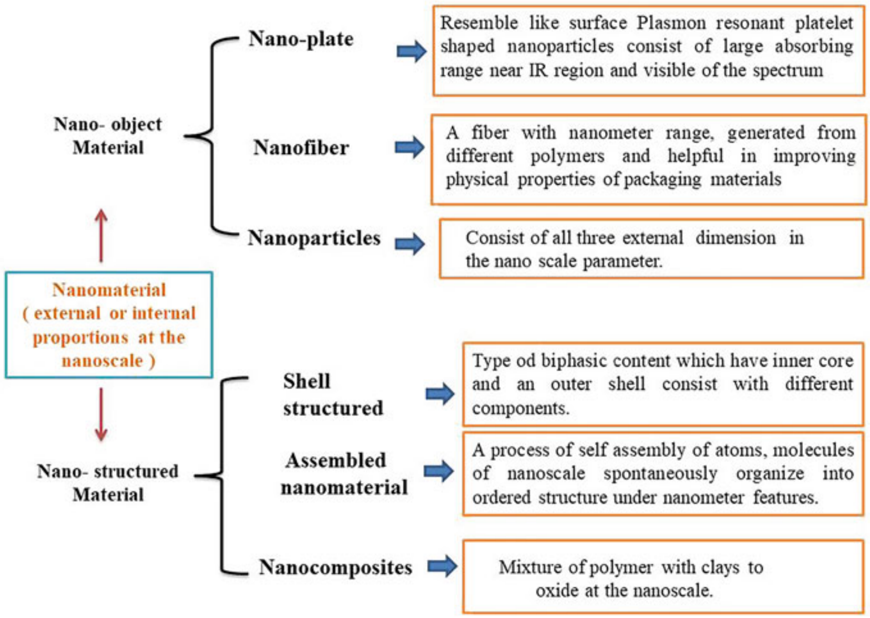

Fig. 10.1 Classification of nano-object materials and nanostructured materials

10.2.1 Physically Improved Nanomaterials-based Food Packaging

Incorporation of nanomaterial to enhance the physical and mechanical properties of food packaging is known as physically improved packaging. To manufacture nano-food packaging material, mixing of nanomaterials into the polymer matrix is an important phenomenon and in addition aids to increase physical characteristics such as gas barriers, temperature resistance, mechanical strength, flexibility, and humidity resistance of food packaging (Vasile 2018). Nanotechnology methods for improving physical and mechanical properties of food packaging are shown in Fig. 10.2.

10.2.2 Nano-Coatings

It is the most common method of application nanomaterials in the form of thin layer or film on the food surface. Nano-coatings are measured in nanoscale thickness ranges from less than 1–100 nm. It is used in covering the surface and also imparting particular physical and chemical functions. Nano coating does not play a role in improving surface topography and is not able to fill cracks or gaps in the surface like paint. Nano coating is formulated by placing one or multiple molecular layers on the surface of basic packaging materials such as glass, metals, ceramic, and polymer (Brody 2006). This film coating acts as a barrier for gases, moisture, and lipids. Edible coating films are directly applied to the food either by liquid film-forming

Table 10.1 Classification of food packaging based on the functions of nanomaterials

Nanomaterials	Physically improved packaging (Brody 2007)	Biochemical improved packaging (Mangiacapra et al. 2006)	Active functions improved packaging (Asadi and Mousavi 2006)	Smart functions improved packaging (Ahuja et al. 2007)
Properties	Utilization of nanomaterial to improve the physical properties of food packaging such as temperature and moisture stability, mechanical power, long durability, gas barrier, and flexibility	Utilization of nanomaterial to improve biochemical properties such as biocompatibility, eco-friendly, edible, biodegradation, and low waste generation	Utilization of nanomaterials with antimicrobial, antioxidant, and UV absorbance properties to improve taste, freshness, and shelf life of packed foods	Utilization of nanosensors to examine and monitor the condition of the food, for example, oxygen indicator, pathogen, and freshness indicator
Type	Nano-coating, nano-laminates, clay nanoparticles, and nanocrystals	Tactoid (phase-separated micro composite), intercalated nanocomposites, exfoliated polymer clay	Antimicrobial function, oxygen scavenging film, UV absorbing films	Freshness nanosensors, oxygen nanosensors, Biosensors for tracking and for active tags
Material	Carbon, metallic, metal oxide, nano-clay nanoparticles	Different types of polymers such as bio-nanocomposites	Silver nanoparticles, metal oxides, and gold nanoparticles	Different types of biosensors
Application	Clay nanoparticles composites are used up to 5% (w/w), these nanomaterials help in 80–90% reduction of oxygen and carbon dioxide permeation	Biodegradable coating film prepared from polysaccharides such as chitosan, starch, pectin, alginate, pullulan, cellulose. These coating materials have good biodegradability, biocompatibility, low waste, and eco-friendly	Prevention of fat oxidation by utilizing metallic iron powder, activated iron, and enhancement of fruit and vegetable shelf life by incorporation of lead-impregnated zeolite, polyvinyl chloride film having ZnO nanoparticles	Toxin (mycotoxin) detection by transducer element tri-layer oxide (SiO_2 10 nm/Si_3O_4 10 nm/SiO_2 10 nm) For microbes detection done by single-walled carbon nanotubes

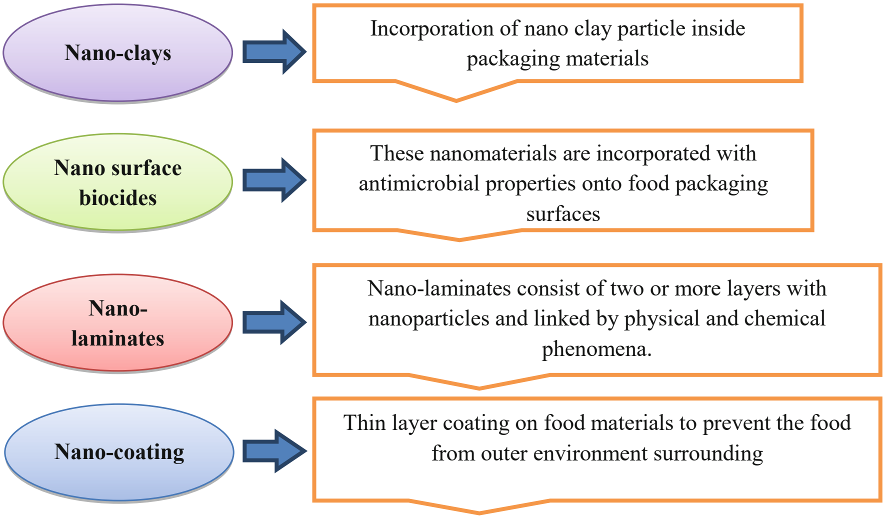

Fig. 10.2 Nanotechnology methods for improving physical and mechanical properties of food packaging

solution or molten compounds (Baldwin et al. 1996). Hydrocolloids, proteins, and lipids are commonly used as an edible coating material for films formation.

10.2.3 Nano Surface Biocide

Specifically utilize nano silver as metallic. For instance: Silver, silver nitrate, zinc oxide, titanium oxide, magnesium oxide, etc. These nanomaterials are incorporated with antimicrobial properties onto food packaging surfaces. They increased shelf life of product, provide significant league quality of mechanical and machinability characteristics. It is the most commonly used packaging for fresh foods and fat-rich products (Guilbert et al. 1997).

10.2.4 Nano-Laminates

Layer by layer deposition of nanomaterials was significantly utilized for edible coating. Layer by layer coating application of active agents was employed between the layers or within the individual polyelectrolytes. Polyelectrolytes with opposite charges interact and deposit by mutual attraction between polymeric activated surfaces and polyelectrolytes having covalent entities. For instance, polyelectrolytes are: bio-based polyelectrolytes (proteins, polysaccharides), lipids (surfactants, phospholipids), colloidal particles (micelles, vesicles, droplets) (Kuswandi and Moradi 2019). Layer by layer phenomena allow integration of active compounds into the films (some instances of active compounds are: antimicrobials, anti-browning agents, enzymes, odor, and flavors) and these agents assist in enhancing shelf life and quality of laminated food commodities (Galus et al. 2020).

Nano-laminates are formulated by dipping and washing. Nano-laminate properties depend on many features such as structure, thickness, and composition, and in addition these characteristics also depend on total dipping steps, varieties of absorbing agents used in dipping solutions and accounting environmental factors which play important role in formulation of nano-laminates (for example, temperature, ionic strength, pH and dielectric constant, etc.). Covalently linked layer by layer films enhanced the modulus and nano-films stability (Kuswandi and Moradi 2019).

10.2.5 Nano-Clays

Nano-clays are defined as clays having nano-size and are significantly employed to enhance the physical properties of food packaging materials. It is utilized in nanocomposites (formation of layered silicates). The presence of silicates in polymer formulation assists in improving diffusive path with the tortuosity (for a molecule to penetrate through it and help in providing better barrier properties) (Bharadwaj 2001).

Nano-clay enhances the polymers mechanical strength and its cooperation with biopolymers enhances the utilization of functional nanomaterial in food packaging. Nano-clays are utilized in a variety of food commodities to enhance the shelf life and stability of food packaging, some instances are processed meats, cereals, boil in bag foods, meat, etc. (Brody 2007). Nanocomposites combine with clays leads in the transport of diffusing molecules are blocked by impenetrable particles/clay and due to this interfacial zones consist of different permeability characteristics as in comparison to basic polymer formed as shown in Fig. 10.3. Consequently, the nonlinear pathway enhances the gas diffusion length, which leads to the prolongation of shelf life of rapidly spoiled foods (Adame and Beall 2009).

The general goal of improved food packaging material is achieved by incorporation of functional nanomaterials into polymer to enhance the mechanical and physical properties. The nano-clay particles are incorporated in different proportions into polymers to enhance the gas barrier properties of the packaging materials for the beverages and oil industry (Table 10.2).

10.3 Biochemical Improved Nanomaterials-Based Food Packaging

Bio-based functional nanomaterials are biodegradable films that are significantly used in food packaging to control the moisture and oxygen transfer as a result it enhances the shelf life, maintain the nutritional values, sensory quality, and safety of foods (Siracusa et al. 2008). As in comparison between plastic and bio-based nanomaterial food packaging, the bio-based nanomaterial seems to be more in favor of eco-friendly nature and in addition to provide best protection to food from

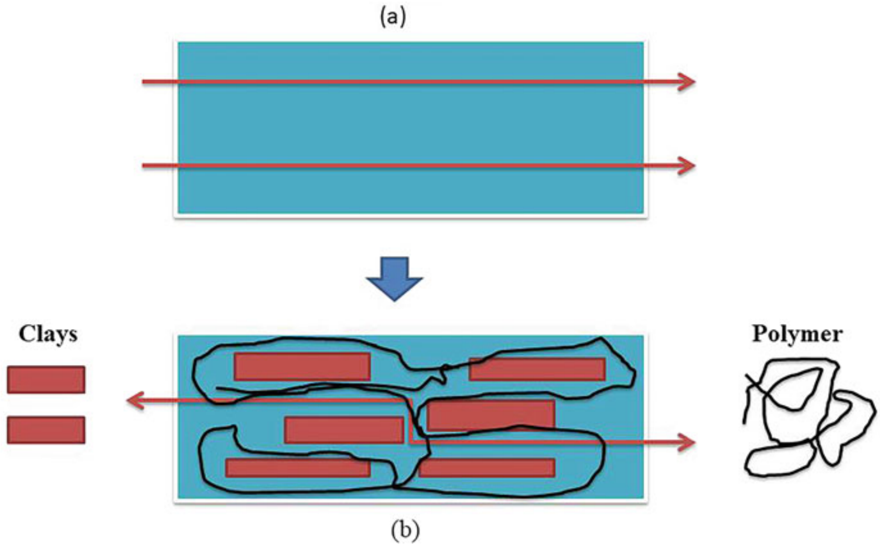

Fig. 10.3 Incorporation of clay nanoparticles into a film matrix

Table 10.2 Effect of nano-clay proportions on food packaging

Nano-clay percentage	Reduction in oxygen permeation	Remarks	References
5% (w/w)	Reduction of oxygen permeation of 80–90%	The properties of the nanocomposites films were significantly improved as in comparison to the material without added clay nanoparticles	Brody (2007)
3% (w/w)	Oxygen penetration is reduced up to 59% and water vapor barrier by 90%	Excess clay loading in ethylene-vinyl alcohol copolymer results in reduction of tensile strength and optical transparency due to clay agglomerates formation	Kim and Cha (2014)
4% (w/w)	Results in increase in oxygen barrier properties	Utilization of (PS) polystyrene to improve oxygen barrier features	Arora et al. (2011)

external environment by preventing it from microorganism growth, gas penetrations, humidity, and to avoid further deterioration of food (Dasgupta et al. 2015). Presenting some instances of bio-based materials that are significantly applicable in functional nanomaterial food packaging systems. The maximum use of polyester (PET; polyethylene terephthalate) for food packaging is prepared from bio-based extracted raw materials (Chandra and Rustgi 1998). In the current scenario it is formulated by using petroleum classified materials and PLA (polylactide) is also biodegradable and its incorporation with nanomaterial enhances the mechanical and barrier properties of food packaging. PEF (polyethylenefuroate) is formulated from 2,5-furan dicarboxylic acid (FDCA) and ethylene glycol both are derived from

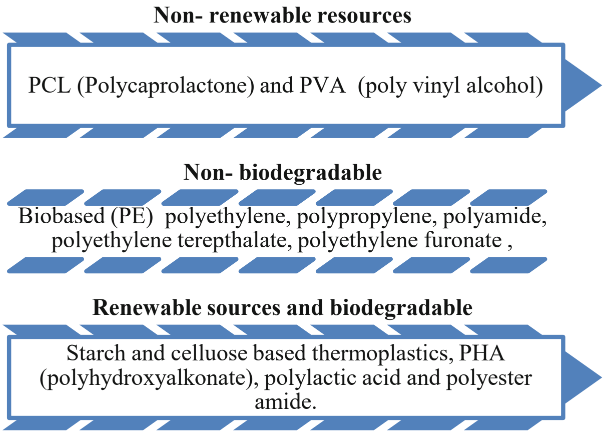

Fig. 10.4 Classification of bio-based material for food packaging applications

renewable resources. The (PTF; polytrimethylenefurandicarboxylate) is made from furan dicarboxylic methyl ester (FDME) and has biodegradable properties. They are successfully utilized for manufacturing of conventional PET, glass, and aluminum bottles. Many of these nanomaterials are not fully eco-friendly but having best sustainability for packaging material (Doi et al. 2002).

Bio-based nanomaterials for food packaging applications are shown in Fig. 10.4 that are easily decomposable in comparison to plastic nanomaterials. Requirement of natural situations such as temperature, oxygen availability, moisture, and biodegradation process of bio-based nanomaterials is a nontoxic phenomenon for the environment (Bhardwaj et al. 2006).

The further classification of biodegradable plastic polymers based on their origin: (a) Biomass-based biodegradable polymer: direct extracted from biomass (polysaccharides, polypeptides, polynucleotide, and protein). (b) Mixed biomass and petrochemical: fabrication of polymer with bio monomers (for instance: polylactic acid/bio-polyester). (c) Production of polymers by microorganisms or GMOs (genetically modified organisms): for example; bacterial cellulose, xanthane, curdin, and pullan (Bhardwaj et al. 2006). The use of nanotechnology in the preparation of biopolymers leads to improve physical and chemical properties of biopolymers and also decreases the overall cost of packaging. The most common nanomaterials used for food packaging are PLA derivates, polyhydroxybutyrate (PHB), chitosan, protein, and cellulose.

10.3.1 Starch-Based Functional Natural Nanomaterials

The convincing characteristics of bio-nanocomposites called “starch-based” having renewable capacity and perfectly fit in a low-cost productive process. Starch-based food packaging can be created to manufacture a film having appropriate mechanical strength. Starch is successfully utilized into a thermoplastic nanomaterial by using extrusion and improves both mechanical and thermal power (Wang et al. 2010). During extrusion process of thermoplastic starch production, plasticizers were applied to lower intramolecular hydrogen bonds therefore helpful in enhancing the stability of packaging material (Abdulmola et al. 1996). The important sources of starch for bioplastic materials are corn, rice, barley, oat, wheat, soy, and potato sources. Starch nature is hygroscopic, therefore their absorbent pads were significantly applied in meat effusions (Park et al. 2002). Starch-based functional films are employed for packaging of both perishable foods and less moisture or dry products (Yoon and Deng 2006).

Due to the hydrophilicity nature of thermoplastic starch (TPS), sometimes it is not appropriate because of the fluctuations in moisture content during processing (Chen and Evans 2005). To overcome this problem nano-filler clay is recommended to improve the TPS property and also enhance the stability of food packaging (Park et al. 2003). The stability of TPS further improved by employing sodium montmorillonite in a concentration of less than 5%. In addition to stability, it also improves decomposition temperature, tensile strength and modulus and reduce relative diffusion coefficient of water vapor (Wilhelm et al. 2003). In recent time, the most common bio-nanocomposites used for food packaging material are starch and its derivates, such as PLA, polyhydroxybutyrate (PHB), and aliphatic polyester, chitosan, proteins, and cellulose.

10.3.1.1 PLA (Polylactic Acid)-Based Functional Nanomaterials

Polylactic acid is produced by chemical processes under a category of bio polyester. PLA is a biodegradable polymer synthesis from phenomena called thermoplastic aliphatic polyester (Chen and Evans 2005). PLA has great capacity in producing a wide range of renewable food packaging materials. The fermentation process is required to manufacture PLA from renewable resources (corn starch) and further polymerization via lactic acid polymerization (Murariu et al. 2008). PLA has good biodegradability characteristics and outstanding mechanical properties (Martino et al. 2006).

The PLA physical and chemical characteristics are based on the ratio of L-PLA and D-PLA. The L-PLA type consists of a high melting point and high crystalline point but a mixture of L- and D-PLA results in an amorphous polymer for the glass transition (Murariu et al. 2008). Some drawbacks are related to PLA, its low reactive side chain constituents decrease its use as packaging element, slow degradation, lower hardiness as well as hydrophobicity. To enhance the mechanical and physical characteristics of PLA, chemical modification is applied by using clay nanocomposite elements (Bandyopadhyay et al. 1999). The clay incorporation with PLA to develop nano-composites of PLA/clay helps in speeding up the process of degradation. Other nano-composites that are also blended with PLAs are silicates (PLA mix with montmorillonites and flurocteroit clays) (Ogata et al. 1997). Moreover, PLA with polycaprolactone is also formed by melt-mixing via advanced kaolinite. All these blended nano-composites PLA has shown significantly great mechanical, gas barrier, and thermal properties in comparison to other polymers without clay (Tang et al. 2008).

PLA incorporation with zinc oxide and silver was employed in different food simulants. Food simulants are part of food elements which reflect the characteristics of food stuffs and in addition this will come in contact with the component of food constituents (Maiti and Batt 2003). Six types of food stimulants are used in migration testing. Stimulant A: 10% ethanol (v/v), Stimulant B: 3% acetic acid (w/v), Stimulant C: 20% ethanol (v/v), Stimulant D1: 50% ethanol, Stimulant D2: Vegetable oil and Stimulant E; poly (2,6-diphenyl-p-phenylene oxide) has particle size 69–80 mesh, pore size (200 nm) (Aguzzi et al. 2007). Food stimulants A, B, and C are utilized for food commodities that have hydrophilic properties (aqueous, alcoholic, and acidic foods) and Stimulants D1 and D2 are employed for food that has lipophilic properties and in addition covers both dairy products and non-dairy products. Stimulant E was utilized for testing specific dry foods. PLA/ZnO; Cu/Ag shows great results in antimicrobial activity in food packaging and also providing great mechanical and thermal properties, barrier to UV rays, water vapor, carbon dioxide, and oxygen (Cabedo et al. 2006).

10.3.1.2 PHB (Polyhydroxybutyrate)-Based Functional Nanomaterials

PHB is an eco-friendly polymeric functional material and formulated by utilizing microorganisms (*Bacillus megaterium*) (Oliva et al. 2007). This functional polymer is utilized as molecule energy storage in the microbial cellular structure. PHB has good biodegradability and biocompatibility characteristics and this makes it fitter for the food packaging industry (Lorz et al. 2000). It is mainly applied for perishable food commodities like fresh meat, dairy products and beverages. In comparison to PP (polypropylene) it has great physical properties and outstanding biodegradable capacity for utilization in food packaging (Lenz and Marchessault 2005).

The microalga *Spirulina species* is involved in synthesizing PHB as a bioproduct and has similar biodegradability rate, mechanical, and thermal characteristics (Weber 2000). Moreover, as this is the byproduct of microalgae, phenolic compounds have antibacterial, antioxidant, and antifungal properties. PHB incorporated with nanofibrils has phenolic compounds and hydrophobicity properties enable PHB nanofibrils to protect food from relative moisture from the surrounding. These nanofibers showed an inhibitory effect on *Staphylococcus aureus* with an inhibitory zone of approx. 7.5 mm. PHB nanofibers produced by the electrospinning process have great barrier to the outer environment due to nonmetric dimensions (Sudesh et al. 2000).

10.3.1.3 Polycaprolactone-Based Functional Nanomaterials

Polycaprolactone is a linear polymer with the semi-crystalline model and high crystalline point and in addition low modulus and high elongation property (Lim et al. 2003). Its biochemical properties are useful for food packaging as well as in biomedical applications and agriculture fields. Due to low melting of polycaprolactone, it is essential to incorporate it with other polymers to increase its stability (Pitt et al. 1981). An incorporation of layer of silicates with the polycaprolactone has developed the nanocomposites which have improved physical properties (Jha et al. 2019).

10.3.2 Cellulose-Based Functional Nanomaterials

Cellulose-based nanomaterials are obtained from lignocellulosic biomass, this has become popular due to its biodegradable and ecological nature. The varieties of nanocellulose materials are employed in food packaging such as cellulose nanofibrils, cellulose nanocrystals, nanocellulose-based hybrid materials, and bacterial nanocellulose. Cellulose nanomaterials had proven good results in reduction in manufacturing costs and also lead as eco-friendly materials. Cellulose nanoparticles are mostly used for food packaging applications, various materials such as in a matrix of alginate, chitosan, PLA, polycaprolactone, pectin, etc. (Khalil et al. 2016). These materials had been incorporated with cellulose nanoparticles by employing different techniques. The nanoscale structure and high surface area of cellulose aids in cellulosic nanocomposites having significantly high mechanical, biodegradation, optical, and barrier characteristics. The effect of different concentration of cellulose nanoparticles on the functionality of packaging has been shown in Table 10.3.

The films made from bacterial cellulose produced from cashew apple juice, and added with lignin (0–15 wt%) and cellulose nanocrystals (0–8 wt%), showed enhanced tensile properties and decreased water vapor permeability (Sa et al. 2020). In addition, cellulose nanocrystals (CNC) combined with super magnetic iron oxide NPs (nanoparticles) were used for the production of high-performance nanocomposites coating films. Soy protein isolate nanocomposites incorporated with CNC and zinc oxide NPs were prepared by different methods and showed good tensile strength, water vapor barrier, water-resistant ability, oxygen barrier, and thermal stability (Xiao et al. 2020).

Table 10.3 Effect of concentration of cellulose nanoparticles on mechanical properties of food packaging

Cellulose nanoparticles concentration (% (w/w))	Mechanical properties	Function remarks	References
5	Tensile characteristics	Enhanced by 42%	Qasim et al. (2020)
5	Water vapor permeability	Reduced by 28%	Qasim et al. (2020)
1	Oxygen permeability	Reduced by 21%	Qasim et al. (2020)
8	Tensile and water vapor permeability	Tensile property increases but water vapor permeability decreases	Rana et al. (2021)

10.3.3 Chitosan-Based Functional Nanomaterials

Chitosan is the second most abundantly found polysaccharide in the world and obtained from many renewable sources. Consequently, it is available at low cost and more commercially feasible. The focused drawback of chitosan utilization as packaging material as in comparison to the non-biodegradable polymers produced from petroleum results in poor mechanical, barrier, and thermal properties (Cazón and Vázquez 2019). The utilization of nanotechnology features aids in improving properties of the chitosan matrix by the combination of newer formulated nanoparticles. Chitosan films are significantly utilized for food packaging materials to sustain the quality of preserved food commodities. Chitosan has high antimicrobial activity which works against a wide variety of pathogenic and food spoilage microorganisms such as fungi, gram-positive and gram-negative bacteria (Kong et al. 2010; Kravanja et al. 2019). The two phenomena used by the chitosan as antimicrobial against: (a) Chitosan successfully bind to the negatively charged bacteria cell wall and leads to the distribution of the cell membrane and also altered the permeability and consequently, inhibiting the DNA replication that results to cell death (Nagy et al. 2011) and (b) chitosan worked as chelating agents that have capability to bound the trace metal and the toxins formulation resulting in inhibiting the microbial growth (Yilmaz Atay 2020). The incorporation of other molecules into the matrix of chitosan-based polymer is proposed for the formulation of new composites film which has significantly high mechanical properties and improved microbial characteristics as depicted in Table 10.4**.**

The major drawbacks of chitosan usage as packaging material in comparison to other commonly used petroleum-based nonbiodegradable polymers are reflected in its poor mechanical, thermal, and barrier properties (Radhakrishnan et al. 2015). The functional properties of chitosan can be improved by the use of nanotechnology with the incorporation of newer nanoparticles, carbohydrates, proteins, and other polymers shown in Fig. 10.5 (Zubair et al. 2020). Therefore, presently, chitosan films are increasingly used as packaging materials to maintain the quality of preserved foods.

10.4 Active Functions Improved Nanomaterial-Based Food Packaging

In active function nano packaging phenomena, nanomaterials come in direct contact with contained food to improve the environment for better protection and enhance shelf life of food commodities (For instance: silver nanoparticles significantly works as an antimicrobial role) (Chaudhry et al. 2008). Moreover, nano-magnesium oxide, nano-titanium dioxide, nano-copper oxide, and carbon nanotubes are also reported as an antimicrobial agent used in food packaging. Commercial production of antimicrobial packaging as oxygen scavengers has been established by Kodak Company (Asadi and Mousavi 2006). Polyethylene films with active enzymes as

Table 10.4 Effect of incorporation of nanomaterials into the chitosan composites

Incorporation of nanomaterials into the chitosan composites	Function remarks	References
Incorporation of titanium oxide and silver having concentration of (0.5%) into chitosan composites	Enhances the water solubility of the film, highest antibacterial property and shows the lowest light transmission of 54.6%, tensile strength was also declined	Lin et al. (2020)
Addition of ZnO and gallic acid into chitosan composites films	Improve the mechanical and physical properties of chitosan composites such as water vapor and oxygen barrier, water solubility, and UV-vis light transmission and also proved to be significantly showing best results in antibacterial and antioxidant activity	Yadav et al. (2021)
Silver NPs/chitosan/PVA	The composite nanolayer is significantly utilized in packaging material for fresh meat with enhanced bioactivity and long shelf life of meat products. The combination of chitosan with nanoparticles shows antimicrobial activity *E. coli, S. entericaserovar Typhimurium, S aureus,* and *Listeria innocua*	Arkoun et al. (2017)
ZnO NPs incorporation into the linseed oil in chitosan/potato-based polymer	Applicable for determination of storage quality of fresh meat and improve the tensile strength and transparency of the film	Wang et al. (2020)
Chitosan gelatin incorporated with nanoencapsulated tarragon essential oil	Applicable for preserving the pork slices. Moreover chitosan incorporation with a variety of essential oils (cinnamomum, assai pulp, thyme, lemon) showed oxidation and microbial growth retardation in a variety of food products	Zhang et al. (2020)

oxygen scavenging function are also reported in the literature and they showed to inhibit microbial growth and ensures the safety of food products (Lopez-Rubio et al. 2006).

Active functional packaging has more advantages over conventional packaging, in that nanomaterials are coated or laminated as antimicrobial agents in order to ensure microbial safety of food products (Lotfi et al. 2018). Antimicrobial films solve the problem of controlling unwanted microbial growth and also reduce health threat microorganisms, mostly those causing contamination on the surface of food products during a post-processing step. The improvement in the functional nanomaterial in the form of active microbial inhibiting functions is a breakthrough process in the food packaging industry for maintaining food packaging sustainability (Kuswandi and Moradi 2019).

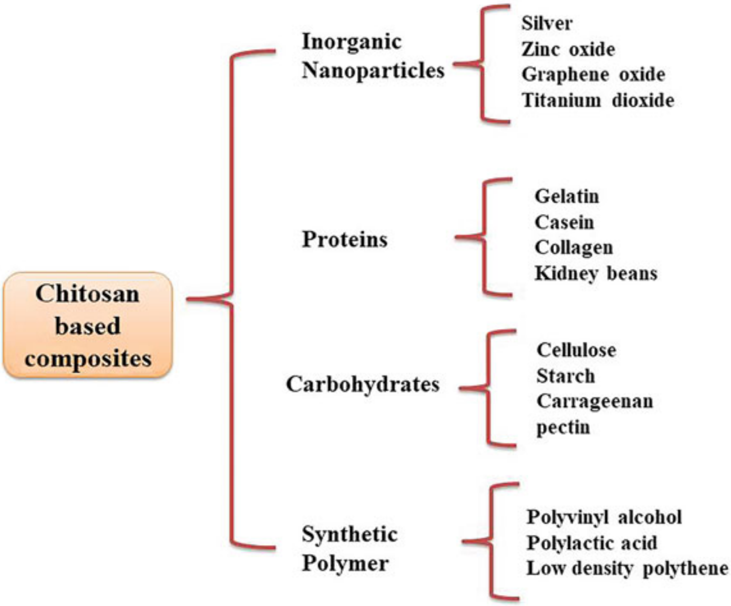

Fig. 10.5 Classification of chitosan-based composites

10.4.1 Antimicrobial Active Packaging

The active antimicrobial function in the packaging mainly consists of the incorporation of antimicrobial agents like silver nanoparticles or silver coatings into packaging materials. These packaging films can minimize the growth of spoilage and pathogenic microorganism. The choice of antimicrobial agents is based on the characteristics of microorganisms such as cell wall composition, oxygen requirements, growth stage, acid/osmosis resistance, optimal growth temperatures, etc. (Malhotra et al. 2015). Different species of microorganisms such as *Salmonella, Staphylococcus, Listeria, Bacillus, Escherichia, Pseudomonas, Lactobacillus, Rhizopus, Aspergillus, Candida,* etc. are responsible for food spoilage (Vilela et al. 2018).

The effective antibacterial characteristics are understood by many molecular mechanisms for instance: production of ROS (reactive oxygen species) having ability to disturb enzyme activity, disturb DNA synthesis, and damage cell organelles as shown in Fig. 10.6. Interactions between cell membrane and nanoparticles are carried by zeta potential present in nanoparticles and this results in cell membrane breakdown influencing the transmission channel through plasma membrane and finally causing cellular death (Gu et al. 2003). Surface of nanoparticles have positive charge and bacterial cell surface comprise with negative charge, this opposite charge responsible for an interaction between enzyme present in bacterial cell and nanoparticles. Therefore, causes cellular death because

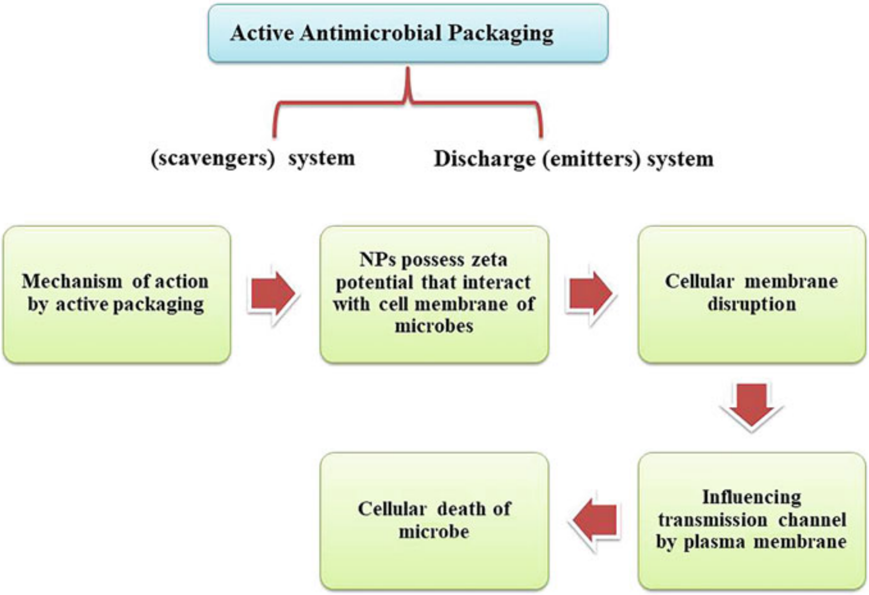

Fig. 10.6 Antimicrobial mechanism of functional nanoparticles

respiratory enzyme present in bacterial cell membrane are destroyed by an efflux-influx of ion inside the cell (Suski et al. 2012). Moreover, signaling chain activates with the interaction of nanoparticles and bacterial cell membrane, for instance ROS production and oxidation of respiratory enzymes that leads to damage of DNA.

The powerhouse of the cell called mitochondria, during ATP synthesis, reduction of molecular oxygen by an ETC (electron-proton transmission cycle), leads the formation of ROS species (superoxide's anions free radicals, hydroxyl, hydrogen peroxide) found to be a threat for microbial species (Yin et al. 2012). It is well discovered that production of ROS results in per-oxidation of cell matters, oxidative stress, disturb communication channels and also generation of protein radicals. Many reported studies proved that nanoparticles such as titanium dioxide devastate the growth of *S. mutants* due to the cohesion of nanoparticles and titanium oxide (Rezaei et al. 2020).

Paracoccusdenitrificans: inhibited by CuO nanoparticles by hampering the enzyme activity of *nitrate* and *nitrite reductase (*Evans et al. 2004*)*. *E coli*: silver nanoparticles hinder the *E. coli* growth, and furthermore ethylene decomposes by silver nanoparticles leads to increased vegetables and fruit shelf life (Shi et al. 2004). Silver nanoparticles are most popular for toxicity to microorganisms, having low volatility and large temperature stability. Titanium oxide, carbon nanotubes, nisin, and chitosan are the other common antimicrobial functional nanomaterials that are applied in food packaging (Chiang et al. 2012).

10.4.2 UV Absorbing Film

Nanomaterial film of nanocrystallineTitania (titanium oxide) utilized as UV absorbing films. The absorbance of t oxide is improved by metal doping and leads to improve its photocatalytic properties under UV radiations. Titanium oxide-coated film treated with UV is most effective to inactivate fecal *E. coli* present in water (Gelover et al. 2006). Doping of titanium oxide with silver nanoparticles and incorporated with PVC (nanocomposites) having great antibacterial characteristics (Cheng et al. 2006).

10.4.3 Oxygen Scavenger Film

Oxygen causes deterioration of many food commodities in a direct or indirect way as it leads to oxidation by direct reactions. Therefore, it is responsible for browning effect of fruits and rancidity effect in vegetable oils. The most common reason for food degradation is indirect reaction by aerobic microorganisms. The problem of food spoilage is solved by integrating the oxygen scavengers into the food packaging materials. So that oxygen scavengers can reduce the oxygen availability and enhances the shelf life of food (Kuswandi and Moradi 2019). Oxygen hunter films are formulated by incorporation of titanium oxide into polymers. These are mainly beneficial for more oxygen-sensitive food products (Xiao-e et al. 2004).

10.5 Smart Functions Improved Nanomaterial-Based Food Packaging

Nanoparticles have a kind of smart functioning in detecting chemical, biochemical, or microbial growth inside the food. Specific microbes and gases nanosensors have been developed for detection of food spoilage (Kuswandi et al. 2011). In this scenario, nanomaterials are employed as reactive materials in food packaging to indicate and communicate the inner condition of packed food commodities, known as nanosensors. Nanosensors are employed to respond as per changes in internal and external parameters of food products and moreover to assure the quality and safety of food (Kuswandi and Moradi 2019).Ongoing research showed that polymeric functional nanomaterials significantly prove to improve the packaging with smart functions (for instance: oxygen determining nanosensors, nanosensors to detect freshness in food, utilization of nano-devices to track the food product and their identification). Nanosensors are capable to detect spoilage of food by change in color parameters due to extreme variation in temperature and humidity with time (Bouwmeester et al. 2009). Inbuilt nanosensors in plastic packaging could detect gases produced by spoiled food and change the package color itself as alarm to the customer about the food quality. Food manufacturing industries predict the shelf life of particular food commodities on the bases of calculating distribution time and storage temperature (Liao et al. 2005). Carbon nanotubes (CNTs) are employed as nanosensors, making the detection process comparatively rapid and precise as compared to the conventional detection process like high-performance liquid chromatography (Nachay 2007). Carbon nanotubes have high-throughput screening capacity, are easy to handle and low cost, less consumption of power, and nice feasibility in recycling. Multi-walled CNTs are significantly utilized in the detection of toxic proteins, microbial growth of specific microorganisms, and food degradation. In the running research scenario, many industries (Nestle, British Airways, and Monoprix) employ nanosensors, useful in the identification of color change under spoilage of food products (Pehanich 2006).

10.5.1 Nanosensors for Freshness Identification

The surfaces of packaging material are laminated with nanosensors for freshness indicator. Electrochemically polymerized conducting polymers such as polyacetylene or polypyrrole are widely used for smart packaging due to excellent change between oxidized over reduced form that is the basis of most of the smart functions (Ahuja et al. 2007). Fish spoilage and microbial growth indication were observed by use of polyaniline film as a nanosensor by color change due to volatile amines produced during spoilage of fish (Kuswandi et al. 2012). This nanosensor aids in indicating spoilage of fish in a constant as well as in fluctuating temperature. The spoilage of food is also done by gas penetration and this is indicated by metal oxides because microbial growth produces gases that are determined by metal gas nanosensor. Nanosensors consist of polymer nanocomposites that have conducting features and are immobilized in a polymeric matrix. Polymer nanocomposites help in detecting gases that evolve from microbial growth (Zhang et al. 2020). The common food-borne pathogens such as *Bacillus cereus, vibrio parahaemolyticus*, and *Salmonella* species are detected by nanosensors based on nanocomposite of black carbon and polyaniline (Arshak et al. 2007). The pattern of chicken freshness was determined by employing metal oxide sensor and responses were further analyzed using neural network (Galdikas et al. 2000).

10.5.2 Nanosensors to Detect Oxygen

Oxygen provides favorable conditions for aerobic microorganisms to enhance their growth and lead to spoilage of food products (Kuswandi and Moradi 2019). Therefore, food manufacturing industries make sure the absence of oxygen in the food package by vacuumed or degassed the package with nitrogen. Nanosensor for oxygen-sensitive foods has been developed by nanocomposite film of titanium oxide and methylene blue. Under ultraviolet radiation, applied nanosensors start bleaching and finally resulted in colorlessness until oxygen is exposed and again blue color appears (Lee et al. 2005).

10.5.3 Nanomaterial Embedded Devices for Tracking and Anti-counterfeiting

Smart functions of nanomaterials are significantly aid in developing tracking devices and anti-counterfeiting to detect the safety of food. The Nanotech Corporations have been involved in the production of nanomaterial-based tracking devices (for instance: Bio silicon) incorporated in the food package to detect the pathogen growth and also easy for customers to identify safe food (Scrinis and Lyons 2007). Nano barcodes are used in each food product, and this is readable by using a microscope for anti-counterfeiting (Roberts 2007). Nowaday's nano barcodes are commercially manufactured by electroplating of inert metal materials like gold, silver, and platinum.

10.5.4 Nanomaterials for Active Tags: RFID

Radiofrequency identification (RFID) is the active electronic information-based systems. It is working on radiofrequency, and used to transfer obtained data from a tag (attached to a packaging material) to automatically trace and identify the object containing particular food products. RFID improves the barcode and manual system of tacking (Abad et al. 2007). Due to the presence of radiofrequency range, long reading ranges have strong capacity to penetrate in adverse conditions like temperature and pressure. Nanotechnology provides nanosensors to work with cheap RFID active tags, called nano labeled RFID tags. The characteristics of RFID tags are: flexible, small printed on external layers of food packaging, and also support low-cost production.

10.6 Techniques to Analyze Functional Nanomaterials

The focused characteristics of nanoparticles are size and shape. To evaluate the surface chemistry of NPs researchers measured the size distribution, degree of aggregation, surface area, and charge (Mourdikoudis et al. 2018). The techniques for characterization of nanoparticles should be fully proven regarding the availability, cost, selectivity, non-destructive nature, affinity to certain material, and simplicity. Techniques needed to understand and used for characterization of NPs have been discussed in Table 10.5. TEM (transmission electron microscopy), SEM (scanning electron microscope), and AFM (atomic force microscopy) are the best instances of microscopic phenomena and used to characterize nanomaterials in terms of size, structure, shape, dispersion, and rate of coagulations state (Pitt et al. 1981). Alone, this technique is not sufficient for complete verification of nanomaterials and it requires other spectroscopic techniques such as X-ray diffraction (XRD) and UV-visible spectroscopy for more accurately characterization of nanomaterials (Jha et al. 2019). Spectroscopic techniques help in the characterization of structure as well as in the analysis of nanomaterials. The XRD is especially employed for the

Table 10.5 Techniques for characterization of nanoparticles

Nanoparticle characteristics	Techniques to characterize NPs
Shape	TEM, AFM, HRTEM, FMR
Size distribution	DCS, DLS, SAXS, NTA, FMR
Chemical state-oxidation state	XAS, EELS, XPS
Growth kinetics	SAXS, NMR, TEM, liquid TEM
Ligand	XPS, FTIR, NMR, SIMS, FMR
Size	TEM, XRD, NTA, SEM
Surface area, specific surface area	BET, liquid NMR
Surface charge	Zeta potential, EPM
Concentration	ICP-MS, UV-VIS, RMM-MEMS, PTA, DCS
Agglomeration	DLS, DCS, UV-VIS, SEM
Optical properties	UV-VIS, NIR, EELS-STEM
Magnetic properties	MFM, FMR

characterization of montmorillonite exfoliation in nanomaterial used in food packaging (Tortora et al. 2002). Quantification of functional nanomaterials in food packaging is also a big evaluating question due to safety reasons. For this scenario migrated nanoparticles can be probed by inductively coupled plasma mass spectroscopy (ICP-MS), inductively coupled plasma atomic emission spectroscopy (ICP-AES), and inductively coupled optical emission spectrometry (ICP-AES).

By utilizing mentioned techniques, nanoparticles up to the size of 0.1–1.0 ppm can be detected (Huang et al. 2015). The determination of heavy metals (Pb, Cd, Cr, Ni, Zn) in food packaging was identified by employing ICP-MS, consequently researchers found the concentration of Pb: 0.023 μg/L, Cd: 0.030 μg/L, Cr: 0.025 μg/L, Ni: 0.012 μg/L, Zn: 0.017 μg/L (Azlin-Hasim et al. 2016). A titanium metal was identified in food packaging by ICP-AES and the concentration was 5.0 mg/kg, the linear dynamic range 100–5000 μg/L and the recovery was 94.7–100.1% observed (Li et al. 2013).

An experiment was conducted on LDPE film coated with three layers of silver precursor at different concentrations 0.5, 2.0, and 5% and migration of silver NPs under different parameters were determined by ICP-AES. The results showed that the mean migration levels ranged between 0.01 and 1.75 mg/L and further the presence of NPs also confirmed by the SEM (Hannon et al. 2016).

10.7 Safety Aspects of Nanomaterials

Food contact articles (FCAs) is a category of functional nanomaterials used in food packaging (Arora and Padua 2010). In FCAs all foods are touched during all stages of production process and transportation. FCAs are combinations of FCMs (food contact materials) such as plastics, papers, metals, board, and glass, and adhesive materials used in ink for printing and coating and in addition functional nanomaterials (Huang et al. 2015). Safety concerns must be fulfilled by determining all food contact chemicals (FCCs) more precisely and including functional nanomaterials that migrate into food commodities and to which consumers are exposed (Alexandre and Dubois 2000).

Food safety is related to human health and environmental health too. The study of migration of nanomaterials present in packaging into food commodities is to assess their potential hazard to environment and human (Duncan 2011). The European legislation reported an overall migration limit of 10 mg per dm square surface area with respect to all substances which have capacity to migrate from nano packaging material to food products (Commission regulation (EU) No. 10/2011) (Cushen et al. 2012). Such as, 1 liter cubic food packaging material with 1 kg of food containing product equal to a migration of 60 mg of packaging material per kg of food product. This criterion is not the same for all food stuffs, it is varied case by case (Foschi and Bonoli 2019). The silver nanoparticle migration from various kinds of nanocomposites into food products has been identified by analytical techniques (Echegoyen and Nerín 2013). In acidic rich food the level of silver migration could happen at a high level and in addition reported that heating is favorable to induce migration and microwave heating showed more pronounce effect on migration. The silver nanoparticle migration can occur by two different mechanisms, firstly by silver nanomaterial getting detached from the composite material and secondly, by silver particles undergoing an oxidation process (Cushen et al. 2013). The silver and copper migration from functional nanomaterials that have antimicrobial action in food packaging is also reported (von Goetz et al. 2013).

The important parameters that would modulate the migration process are nanofillers present in nanocomposite materials, contact time, and particle size. Researchers are more focused on less migration of silver ions into food stuffs; this model benefits the industry regarding decreasing cost and time in migration process studies (Cushen et al. 2014). An incorporation of PLA (polylactic acid) nanocomposites and organo-modified clay utilized an FCM and found that migration of ions into water was less than 10 mg per dm square of the functional nanomaterials (Maisanaba et al. 2014a). Moreover, rats were also exposed for 90 days to the extracts of migration in drinking water and results showed that migration extracts from nanoparticles did not show toxicity, for instance, inflammation or oxidative stress. This defined evidence proved that nanomaterial migration into food stuff was high as in comparison to migration into water (Maisanaba et al. 2014b). Functional improved nanomaterials are needed to investigate more and make sure of the safety of nanomaterials application in the nanoparticle-based food packaging industry (Maisanaba et al. 2014a).

Three important regulations are undertaken to make sure that nanomaterials used in food packaging have high standards for safety of food, safety of consumer, and safety of environment (Jorda-Beneyto et al. 2014). Moreover, these all are essential requirements for successful utilization of functional nanomaterial for the food packaging industry and also having special investigation knowledge regarding; nanomaterials toxicological effects, migration of ions into foodstuffs and their exposure level in working place and consumers (Houtman et al. 2014). If these three regulations were followed properly with all guidelines, nanomaterial for food packaging would become safer, healthier, and tastier as well as more nutritious with eco-friendly nature (Maisanaba et al. 2014a).

10.8 Conclusion and Future Potential

The current investigation results showed that nanotechnology provides a number of opportunities in functional nanomaterial in food packaging ranging from bio base to smart packaging. The important beneficial parameters that make nanomaterials more suitable for food packaging are: significantly stronger role, lighter, more durability, and also enhances shelf life of food commodities. Moreover, positive effects on health and low production cost. To develop new food packaging features, nanotechnology proves to increase food characteristics (healthier, tastier, delicious, and full with more nutritious value). The nanosensors incorporation as intelligent packaging provides the food state inside packaging material with visual information. Nanosensors are advantageous to consumers by alerting them when food material inside the packaging material is already spoiled. The conventional food packing system is changed by smart functional nanomaterial food packaging. The future packaging of food materials is safer, healthier, and less harmful to the environment. Nanomaterial food packaging is beneficial for preservation of perishable food products. By utilizing smart and active nanomaterial for food packaging, it could support the food packaging with better mechanical properties; provide stronger barriers from the external environment and better thermal properties. For example, nanomaterial utilized food packaging avoids bacterial invasion and growth for safety of food.

The conventional method of food packaging by biodegradable and natural polymers is not sufficient to provide better safety and healthier food commodities to the consumers due to their poor mechanical and barrier properties. Incorporation of nanofillers (clay) into biopolymers provides a path to improve in general performances (mechanical, thermal, and barrier properties). Despite all positives of nanomaterial function in food packaging, their proper use for packaging may develop safety concerns to human health due to their different physicochemical properties from their macroscale properties. More infestations are needed to understand the impact of nanomaterial or nanoparticles on human health and in addition research should also be focused on identification, quantification, and characterization of functional nanomaterials. Migration of nanomaterial ions into food commodities is a crucial point to understand functional nanomaterial for food packaging. Nanotechnology in the food packaging industry is in its infant stage, more research and investigations are needed to make functional nanomaterial more feasible for food packaging regarding safety, health, and environmental concerns.

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Rules and Regulations Related to Packaging 11

Amrita Bhanja and Monalisa Mishra

Abstract

There is a rapid growth in the food supply chain starting from the manufacturing to packaging and distribution. These processes in one or the other way can damage or hamper the product quality at any stage of handling. Therefore, proper packaging is the right way to protect the product from different stresses that would eventually extend the shelf life of the product satisfying the consumers need. This chapter basically deals with the rules and regulations related to the packaging as per the Ministry of Health and Family Welfare, regulated by the Food Safety and Standards Authority of India (FSSAI). It briefly provides information regarding the types of packaging materials suitable for a specific product while packaging. Along with that, the factors responsible for affecting the food quality and the innovative techniques of packaging are also discussed in this chapter.

Keywords

Packaging material · FSSAI · Regulations · Food quality · Quality degradation

11.1 Introduction

The growing interest of consumers towards processed or ready-to-eat food have been attracting the food industries and markets to produce the type of food that would store for several days without any quality degradation and wastage. With the

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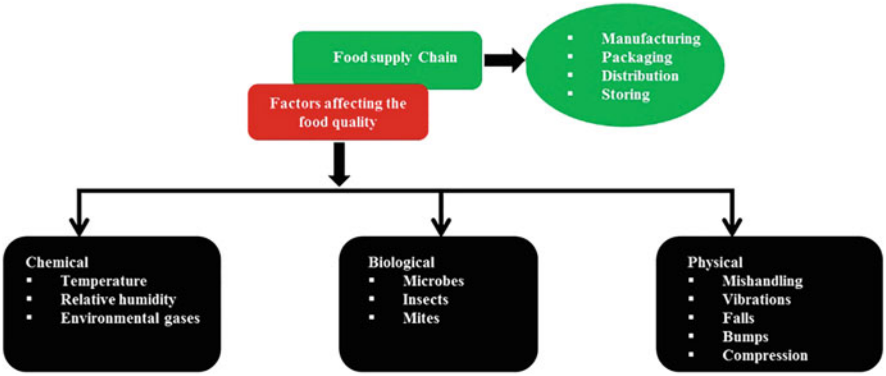

Fig. 11.1 Schematic diagram showing the processes of food supply chain and the factors affecting the food quality during these processes

increasing demand for the processed food, it also targets the safety of the food throughout the supply chain since the wastage and quality loss of food is a very common and frequent problem starting from its manufacturing, transportation and distribution process. As per the information given by Food and Agriculture Organization (FAO), around 1.3 billion tons of food approximately are found to be wasted during the food supply process (Chen et al. 2020). Thus, to cope up with the consumer's demands, it is very much necessary to process and pack the food in a way so that it gets least affected by different environmental factors, mishandling, transportation, etc. Proper packaging not only protects the food from the outside damage, but also it is efficient enough to retain the nutritive quality extending the shelf life of the food. In other words, packaging is also done to neutralize the negative reactions that might affect the stability of the packed food (Gilbert 1985). Along with this, a proper packaging should contain all the relevant information like the manufactured and the date of expiry, the composition, and quantity of the contained food. Above that, it should be approved by the FSSAI (Lamberti and Escher 2007). The type of material plays a very crucial role, when it comes to the process of packaging. Plastic is the largely used packaging material as it not only provides the necessary safety to the food but also can be modified and incorporated with different other materials that would enhance the quality of the food. On the other hand, plastics are non-biodegradable substances that have become the main reason for the global waste problem. It has been badly affecting marine life along with animal and human health in a large ratio which has become a great matter of concern (Lu et al. 2019). Therefore, it is very much necessary to reduce the single use of plastic and promote ways that would balance the utilization of plastic as a packaging material along with its disposal measures. This chapter provides information about the recent rules and regulations formulated by the FSSAI regarding the packaging materials to be used for specific products (Fig. 11.1).

11.2 External Factors Influencing the Quality of the Food

The main purpose of packaging the food is to prevent its quality from getting deteriorated, extending its shelf-life. Proper packaging of the food helps to retain its quality by protecting it from the outside environment which includes several factors like biological changes (microbial contamination), damage caused from the transportation, any sort of theft and manipulation of the product during transportation, and climatic changes that could negatively influence the compositional and nutritional quality of the product (Yildirim et al. 2018). External factors that may hinder the quality of the food can be categorized into chemical, biological and physical factors.

11.2.1 Chemical Factors

Exposure to different environmental conditions, like temperature, relative humidity and environmental gases, plays a major role in degrading the quality of the unpacked or not properly packed food (Marsh and Bugusu 2007). Temperature plays a very crucial role in maintaining the quality of food. The effect of factors like temperature and relative humidity on fruit and vegetable has been explained (do Nascimento Nunes 2008). Direct contact of unpacked fruits and vegetables with the excess amount of atmospheric temperature may deteriorate their nutritional quality, texture and appearance. The deterioration of the quality increases constantly by two to three folds with the elevation of the temperature at every 10 °C (Qin et al. 2014). In order to minimize the quality deterioration, postharvest conditions such as temperature management, storage, along with adequate knowledge of the packaging material have to be given priority. Like temperature, the ambient relative humidity is also a matter of concern when it comes to the quality of unpacked food. The water vapour pressure between the surrounding and the product is affected by the humidity along with the temperature. To balance and minimize the level of water vapour pressure loss, the surface humidity has to be maintained in order to prevent the loss of moisture that takes place due to the process of transpiration. As a result, the moisture loss can be neutralized and maintained by controlling the movement of the surrounding air between the food and the environment by using different protective layers or appropriate packaging. The use of proper packaging materials like glass, plastics or film wrapping may prevent the moisture loss from the product by increasing the surface relative humidity. The increased amount of oxygen in the environment could damage the quality of the food by increasing the reactive oxygen species (ROS), damaging the cytoplasm and hindering metabolic activities (Choudhury et al. 2017). There is a high chance of rancidity (Li et al. 2014) and colour degradation (Teixeira et al. 2016) of the fruit due to the low oxygen and high carbon dioxide concentration respectively. Therefore, different products require different atmospheric conditions under modified atmospheric packaging (MAP) (Belay et al. 2019).

11.2.2 Biological Factors

Fermented foods are becoming more prone to microbial contamination as compared to fresh products due to mishandling, unhygienic environment and exposure to contaminated water. These fermented foods without appropriate packaging serve as a niche for the bacteria and fungi leading to different intoxications and foodborne illnesses (Roy et al. 2007). As it is previously been mentioned that unpackaged food are more affected by high temperature, likewise packaged food are highly prone to warm temperature. Even though the food is protected by packaging, there are several studies revealing the inefficiency of the poor quality packaging material. Protecting and maintaining the quality of the foodstuffs for longer period of time from being easily affected by insects, mites and microbes is a great matter of discussion as not all packaging are safe and appropriate for the product. Packaging should be done depending on the type and quality of food. Different products require different packaging. Packaging material used should be capable of avoiding infestations by mites and insects. Like unpackaged product, low-quality packaging or poor packaging is equally responsible for affecting the product. A small damage in the packaging material may allow the pest to enter the food followed by the quality deterioration. A chemical known as pheromones released by the pest helps them to increase their rate of population by approximately 20–30 folds every month if they get favourable conditions. This may lead to direct rejection of the whole product raising several legal consequences for the entire chain (Bell 2011).

11.2.3 Physical Factors

Physical factors are the damages that may take place during the handling, storing, transportation and distribution of food products. Such damages include vibrations, falls, bumps and compression that could take place during the process of transportation. Therefore, packaging is considered to be a very basic as well as an important parameter for maintaining the safety of the food products (Robertson 2012a).

11.3 Impact of Packaging

Starting from the manufacturing, handlings, storing of the fresh and processed food products till the distribution to the consumers, all the processes are carried out with proper standard operating procedures (SOPs) from the government. There are several amendments published by the FSSAI regarding the packaging of the specific food products. The recent amendment that was generated by the FSSAI regarding the rules and regulations of packaging was in the year 2018. The packaging material is chosen depending on the type and quality of food products in order to avoid the degradation of the food. Some of the materials that are commonly used for packaging are cardboard, glass, metal, plastic, etc. (Robertson 2012b). Airtight containers are used for packaging processed vegetables and fruits that would resist the oxygen

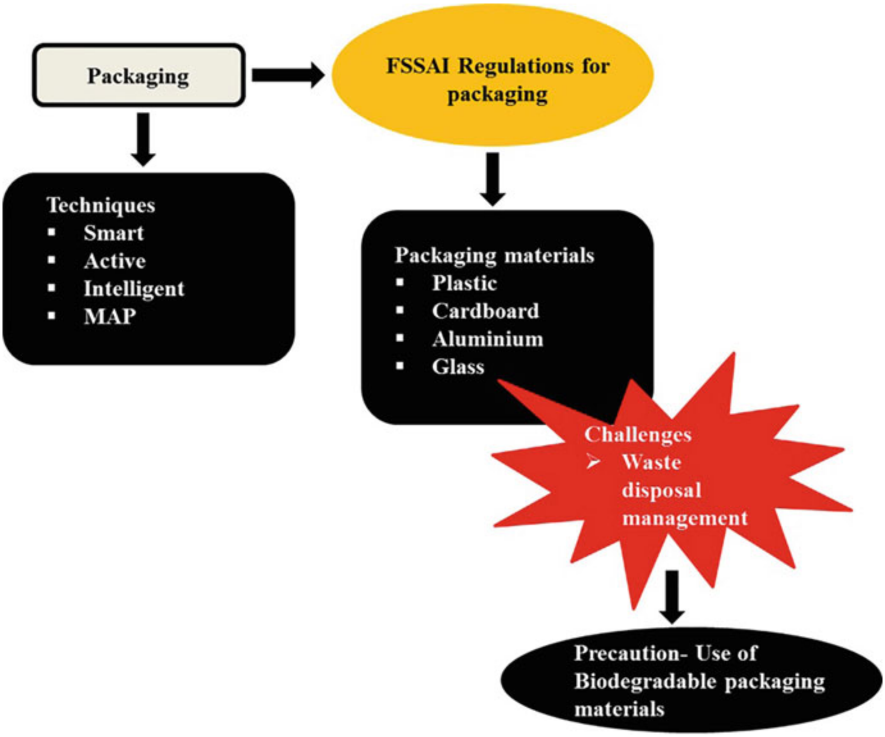

Fig. 11.2 Schematic diagram showing the overall view of packaging

transmission responsible for product spoilage due to microbial contamination and lipid oxidation (Robertson 2009). The liquid products are packaged using glass jars and bottles whereas the solid stuffs are usually packed by cardboards and plastics. Almost 70% products are packed in the food industry of which around 48% of the total packaging is made from the paperboard (Opara 2013) (Fig. 11.2).

11.4 FSSAI Regulations for Packaging

All the rules, regulations and the decisions regarding the food are implemented by the FSSAI, Government of India. Recently the regulations vide no F.No. 1-95/Stds/Packaging/SP(L&C/A)/FSSAI-2017 under sub-section (1) of section 92 of Food Safety and Standards Act, 2006 (34 of 2006) regarding packaging was published and made available for the public in the year 2018 (FSSAI 2018). Some of the important regulations from the above-mentioned document have been mentioned here very briefly.

General requirements that must be followed by the food business authorities regarding the packaging material are that the packaging material should be (of):

- Food grade quality
- Suitable for the product
- Withstand mechanical, chemical and thermal stress
- Hygienic, clean and tamper-proof
- Compatible sealing material
- Not to re-use tin containers
- Printing inks (IS: 15495 conformed)
- Food products not to come in contact with the printed surface
- Not to use newspaper for storing and wrapping
- The layer in the multilayer packaging that would be coming in contact with the food should conform to the necessary requirements of the packaging material

11.5 Packaging Materials Suggested by FSSAI to Be Used for Specific Product

According to the rules of FSSAI vide no F.No. 1-95/Stds/Packaging/SP(L&C/A)/FSSAI-2017 published in the year 2018 (FSSAI 2018), there has been a list of packaging materials that are suggested to be used for specific food products. Some of them are being mentioned here very briefly (Table 11.1).

11.6 Innovative Techniques of Packaging

The innovation of different modern techniques has made the packaging system more valuable and informative, providing the necessary information regarding the quality of the food in their packaged form. Such types of packaging are provided with smart sensors and indicators to monitor the quality. Apart from this, the environment of the packaging materials is modified and incorporated with the required edible material coming in direct contact with the food resulting in the quality enhancement of the product. Some of the innovative packaging techniques are discussed below.

11.6.1 Smart Packaging

Smart packaging is a broad concept and can be categorized mainly into two types of packaging like active and intelligent packaging. The intelligent packaging works by monitoring the external and internal alteration of the product (Vanderroost et al. 2014). The ultimate purpose of smart packaging is not only to keep up the quality and the storage life of the food product, but also to reduce the overall food waste and loss by using several modified techniques, detectors and hardware elements that have been briefly described in active packaging and intelligent packaging. This trending system of packaging is being applied and used by food and pharmaceutical industries to improve and extend their food supply business in a convenient, safe,

Table 11.1 FSSAI regulations regarding the use of packaging materials for specific products

Sl. no	Food products	Materials used for packaging
1	Milk	• Glass bottle + metal caps/plastic caps (polypropylene (PP) or high-density polyethylene (HDPE)) • Plastic container of polyalkylene terephthalate (PET) + PP or HDPE caps • Plastic container of HDPE/PP/polystyrene (PS) + PP or HDPE caps (Food Safety and Standards (Packaging) Regulations 2018). • Flexible plastic pouch of polyethylene (PE) or PP-based multi-layered packaging • Aseptic/flexible packaging material of paper board/ aluminium foil/polyethylene-based multi-layered structure • Container made of tin plate (Food Safety and Standards (Packaging) Regulations 2018a) • Plastic cups made of (PP or PS) + paper/peel-off lid • Paper butter wrappers coated with wax • Metal containers + plastic PP caps/metal/plastic lid • Plastic pet container + plastic lid • Thermoform cup/tray + paper/peel-off lids (Food Safety and Standards (Packaging) Regultions 2018) • Packaging material made of paper and paper board with/without plastic film lamination, greaseproof paper • Mud or clay pots
qx	Fats, oils and fat emulsions	• Container made of tin plate • Glass bottle + metal caps /plastic caps (polypropylene (PP) or high-density polyethylene (HDPE)) • Plastic container/jar of HDPE • Plastic bottle/jar (PET) + plastic caps • Plastic pouch (multi-layered laminated or co-extruded structure • Aseptic/flexible packaging material of paper board/ aluminium foil/polyethylene-based multi-layered structure • Plastic laminated pouch (Food Safety and Standards (Packaging) Regulations 2018) • Thermoform plastic jar + plastic caps
3	Fruit and vegetable products	• Glass bottle + metal caps/plastic caps (polypropylene (PP) or high-density polyethylene (HDPE)) • Can be made of aluminium with an easy open end • Container made of tin plate • Aseptic/flexible packaging material of paper board/ aluminium foil/polyethylene-based multi-layered structure • Plastic jar of HDPE/co-extruded with plastic (PP/HDPE caps) • Flexible plastic pouch of (PE/laminated structure) • Plastic jar + metal caps • PET/PP/PVC Punnets (Food Safety and Standards (Packaging) Regulations 2018a)

(continued)

Table 11.1 (continued)

Sl. no	Food products	Materials used for packaging
4	Sweets and confectionary	• Metal containers + plastic PP caps/metal/plastic lid (multi-layered laminated heat sealed pouches) • Composite containers prepared of paper board/ aluminium foil/plastic based films + plastic/metal lids (Food Safety and Standards (Packaging) Regulations 2018a) • Foil wrap • Plastic film based twist wraps (PET/PP/PVC) • Thermoformed tray/punnet + lid • Glass bottle + metal/plastic caps • Plastic cups + film lid
5	Cereals and cereal products	• Tin container • Aluminium foil-based laminated pouch in metal container • Wrapper of wax-coated paper (Food Safety and Standards (Packaging) Regulations 2018b) • Plastic heat-sealed multi-layered laminated pouch • Plastic thermoform container + plastic lid • Plastic multi-layered laminated Zipper pouch • Thermoform trays + plastic lids/over wraps • Glass bottle + metal caps • PET/plastic-based rigid containers + metal/plastic caps ((PP) or (HDPE)) • Plastic/co-extruded film/PP/PE
6	Meat/meat products/poultry products	• Glass jars + plastic (PP)/(HDPE) caps • Metal containers + metal lid (lacquered tin containers) • Plastic flexible pouches in paper/paperboard carton • Overwrapped plastic tray • Aluminium foil wrap • PET punnets/containers with plastic caps(Food Safety and Standards (Packaging) Regulations 2018)
7	Fish/fish products/seafood	• Glass jars + plastic caps (PP/HDPE) • Metal containers + metal lid (lacquered tin containers) • PET punnets/containers with plastic caps (Food Safety and Standards (Packaging) Regulations 2018b) • Plastic heat-sealed multi-layered laminated pouch • Overwrapped plastic tray
8	Honey and other sweetening agents	• Glass bottle + metal caps /plastic caps (polypropylene (PP) or high-density polyethylene (HDPE)) (Food Safety and Standards (Packaging) Regulations 2018) • Plastic based thermoformed containers • PET container + plastic caps • Laminated tube of plastic
9	Salt/spices/condiments	• Glass bottle + metal lid/plastic caps (PP + HDPE) • Plastic container + plastic cap (PET + HDPE) • Plastic heat-sealed multi-layered laminated pouch
10	Beverages (excluding diary/ fruits/vegetables based)	• Plastic bottles made of PET/polycarbonate (PC) + plastic (PP/HDPE)/aluminium caps

(continued)

Table 11.1 (continued)

Sl. no	Food products	Materials used for packaging
		• Heat-sealed plastic pouch made of PE • Glass bottles + metal/plastic caps • Plastic pouch made of PE in corrugated fibreboard boxes • Aluminium can have an easy open end • Container made of tin plate (Food Safety and Standards (Packaging) Regulations 2018a) • Wooden cask (for wines)

and in a better way in order to minimize the large amount of loss (Janjarasskul and Suppakul 2018; Poyatos-Racionero et al. 2018).

11.6.2 Active Packaging (AP)

Active packaging is introduced as a well-planned, effective and chemical approach to protect and extend the quality and shelf life of the food (Qiu et al. 2019). The chemicals used in active packaging are not added directly to the food rather they are incorporated into the packaging materials. As per the definition given by the European regulation (EC) No 450/2009, active packaging is the packaging that uses "*deliberately incorporate components that would release or absorb substances into or from the packaged food or the environment surrounding the food*" (Commission E 2009). This type of packaging involves the incorporation of a chemical compound either absorbers or emitters to the packaging materials. One such example of the chemical that is commonly used is the oxygen absorber. The former scavenging systems (absorbers) absorbs the excess or unwanted compounds like moisture, ethylene, oxygen, carbon dioxide of the food to the environment that helps to extend the shelf life of the product. On the other hand, the emitters or the releasing systems help in adding the compounds like antimicrobial compounds, ethylene and antioxidants from the environment to the food ultimately balancing the packaging environment, extending the shelf life of the product (Yildirim et al. 2018). One such application of active packaging is that it was used to retain the colour of the chicken breast at 4 °C for 60 days (Stratakos et al. 2015).

11.6.3 Intelligent Packaging

As mentioned earlier, intelligent packaging is another form of smart packaging that uses various hardware and electronic devices to monitor the internal and external conditions of the packaged food product (Kruijf et al. 2002). It provides information about the products during their transportation and storage (Kerry et al. 2006). Through this system of packaging, it becomes easy to monitor the parameters like microbial contamination, temperature, and product purity. Along with this, it also gives information about the changes due to the pH and enzymatic reactions through the Vitsab time-temperature (TTI) indicator (Opara 2013). It also incorporates radio-frequency identification (RFID) devices that would provide data about the pH, food volatiles, gases, and conductivity with the use of chemical elements (Chen et al. 2020).

11.6.4 Modified Atmosphere Packaging (MAP)

The modified atmosphere packaging can be explained in a way where the atmosphere surrounding the food inside the packaging can be altered or modified as per the requirement so that it will not affect the shelf life along with preventing the quality of the food. It basically works on inhibiting the microbial contamination and stops the enzymatic spoilage. The packaging is made up of semi-permeable films in such a way that it tends to lower the exchange of the respiratory gases inside the package (Chitravathi et al. 2015). Along with carbon dioxide, which is known for its antibacterial ability (Sun et al. 2017), oxygen and nitrogen are also used. Specifically, these are the three gases that are used for the packaging for extending the shelf life of the food in MAP. The ratio and the composition of the gases completely rely on the type of food. Every food has its own environmental stability. Nitrogen is basically used as a filler gas. Several studies have been carried out that proved the efficiency of MAP. This method was successfully used for packaging smoked catfish without influencing its organoleptic qualities (Qiu et al. 2019).

11.7 Materials Used for Packaging

The selection, construction and designing of the packaging material play a key role in maintaining the storage life of the product. The material to be used for the product should be efficient enough to retain the quality, originality and the freshness of the product throughout the food supply process. Paper, aluminium, glass and metal are some of the traditionally used materials. Along with this, plastic has been the highly used packaging material that is being used in several forms.

11.7.1 Plastic

The use of plastic as a packaging material is the most utilized and given the topmost priority in the food industries. It is the highest utilized packaging material all over the world. Apart from the well-known disadvantages, there are a lot of advantages that makes it liable as a packaging material. Thermosets and thermoplastics are the two categories of plastics used for different purposes. Amongst them, thermoplastics are used for the packaging of food because of their flexible nature of getting easily moulded into different shapes and sizes depending on the type of food (Marsh and

Bugusu 2007). As compared to the other packaging materials like aluminium and metal, plastic provides more transparency that makes them easily visible to the consumers in spite of the packaging (Opara 2013). They are considered to be of lightweight, chemically inert, easy to print and handle as compared to the other packaging materials. The major concern that raises question regarding the frequent use of plastic includes health as they contain plasticizers and stabilizers and environmental problems as these are non-biodegradable substances (Marsh and Bugusu 2007). Its effective barrier property makes it microbiologically safe (Lamberti and Escher 2007).

11.7.1.1 FSSAI Regulations Regarding Plastic as Packaging Material

Food products packed using plastic shall obey the Indian Standards specifications

- Packaging of the drinking water shall be done using transparent, tamper-proof bottles conforming to.
- IS: 9845—migration limit (60 mg/kg or 10 mg/dm^2)
- It also provides the migration limit (mg/kg) of the substances like barium, cobalt, copper, iron, lithium, manganese and zinc from the plastic materials
- IS: 9833—for pigments to be used in plastics
- Not to use recycled plastic products for packaging, carrying and storing of food (Table 11.2)

11.7.2 Paperboard

The recyclable, eco-friendly and inexpensive nature of cardboard makes it reliable for using it as a packaging material. In the food industries mostly cardboards are used in the form of cartons for packaging freshly produced fruits and vegetables. Sulphite and sulphate are used to convert cellulose fibres obtained from wood into valuable paper and cardboard (Robertson 2012b). Cardboards are made up of a wide range of plain paper. A normal plain paper is not utilized for packaging purpose as they are inefficient in preserving the food for a long time. Therefore when used for packaging, it is added with some materials like resins, wax to improve its strength. As compared to the paper, paperboard is of more strength (Marsh and Bugusu 2007).

Table 11.2 FSSAI standards for specific plastic materials

Indian Standards specifications (IS)	Material
IS: 10146	Polyethylene (PE)
IS: 10151	Polyvinyl chloride (PVC)
IS: 12252	Polyalkylene terephthalate (PET)
IS: 10910	Polypropylene (PP)
IS: 14971	Food grade polycarbonate
IS: 10142	Polystyrene

11.7.2.1 FSSAI Regulations Regarding Paper and Board as Packaging Materials

- Should maintain uniform thickness
- Free of grease marks, pinholes, cuts
- Should be contaminant free and be of food grade
- Should conform to Indian Standards Specification

11.7.3 Aluminium

Aluminium is one of the most highly available metallic constituent of the earth. It is silvery white and malleable in nature. It is expensive and used for preparing different seamless containers. According to Morris, 2011, it is mostly used for packaging sea food (Morris 2011), and soft drinks (Deshwal and Panjagari 2020). Mainly aluminium is used in the form of aluminium foil in the food industries for packaging as it prevents the light to pass through it and retains the original moisture, aroma and gases of the food. When it comes to the toxicity of aluminium, it is safe as a packaging material. It is of lightweight and can be moulded into different shapes as demanded by the nature of the food. The benefit of using aluminium as a packaging material is that it is recyclable, environmental friendly and obtained in the same quantity after being recycled(Lamberti and Escher 2007).

11.7.3.1 FSSAI Regulations Metal as Packaging Material

Containers shall be considered unfit for human consumption, when the metal (packaging material) shows the following characteristics:

- Rusty
- Enamelled, chipped
- Not properly tinned copper or brass containers
- Should use appropriate grades of metal for packaging
- Shall conform to Indian standards specifications

11.7.4 Glass

Glass is another most frequently used packaging material. It is mostly used for packaging soft drinks, juices, pickles and many more. It tends to be a permanent kind of packaging material that is reusable. It is considered as a highly useful packaging material as it is chemically inert, recyclable and easily manufactured from raw materials (Le Bourhis 2008). Apart from the above-mentioned advantages, there is a disadvantage of requiring a lot of raw materials for its production like silica, dolomite, and also consumes a lot of energy (Patrascu et al. 2009; Kovacec et al. 2011).

11.7.4.1 FSSAI Regulations Regarding Glass as Packaging Material

- Should be free from blisters, stones, chippings, mould marks and visible defects
- Should be of smooth surface without cracks, sharp edges and pinholes
- Sealing surface should be crack free

11.7.5 Incorporation of Edible Films in the Packaging Material

In order to prevent or lower the quality deterioration of fruits and vegetables caused due to the water activity and the ambient temperature, packaging incorporated with hydrocolloids could be a better option for using it as oxygen barriers (Robles-Sánchez et al. 2013). The use of edible packaging was also applied on several foods to safeguard their nutritional and organoleptic properties. These sorts of packaging help in neutralizing the antioxidant activity along with reducing the oxygen permeability. The use of such edible films in the food products works as an oxygen barrier that would eventually prevent or reduce the oxidation of lipids, flavours and colorants. Such oxygen barrier may also delay the process of respiration in the fresh produce especially fruits and vegetables. Different types of modifications like the use of synthetic nanofibres, carbon nanotubes and nano clays can also be implicated in these edible films as well as coatings that would improve the oxygen barrier properties. Polysaccharides and protein edible films can be used as good and effective oxygen barriers as they are known to carry antioxidants that would migrate towards the surface of the food. The oxygen permeability is influenced by different environmental properties as well as packaging conditions like temperature, film thickness, relative humidity and moisture content (Gómez-Estaca et al. 2009a, b). The oxygen permeability tends to decrease with the lower humidity as the structure of the film remains intact. There are studies showing the increase in the oxygen permeability due to the increase of the humidity when plastic films were used to coat the whey protein (Hong and Krochta 2006). Like humidity, increase in temperature also leads to the increase of oxygen permeability. This may reduce the extended shelf life of the food product. The use of antioxidants in edible coatings and film may reduce the process of rancidity, discoloration and degradation. Natural antioxidants extracted from the plants can also be incorporated to films that would result in the production of biopolymers having antioxidant activity. The oxygen permeability is directly influenced by the thickness of the film. According to (Bonilla et al. 2012), the oxidative reactions are affected by the factors like continuity and homogeneity of the films. Excess light exposure can lead to photo-oxidation of food. So packaging incorporated with low light permeability film like hydroxypropyl methycellulose can be used while packing products like fats and oils. The utilization of such films is helpful in reducing the process of photo oxidation (Akhtar et al. 2010). Apart from the above-mentioned coating, there are several other coatings like gellan, alginate and pectin-based edible coatings that were used to coat fresh-cut melon. These coatings were useful for reducing the level of dehydration. They were also effective in preventing ethylene production resulting in the reduction of carbon dioxide along with oxygen permeability. Using alginate and pectin coating reduced the wounding stress (Oms-Oliu et al. 2008). Chitin derived from the yeasts, insects, fungi and invertebrates after deacetylation forms chitosan (Dehghani et al. 2018) that can be used for film formation due to their unique nature of toughness and biodegradability (Sahraee et al. 2019).

11.8 Challenges

Despite several advantages regarding the use of the packaging material especially plastic, it has come up with a lot many challenges that are eventually and immensely affecting the earth in some or other ways. This global problem is not only affecting the terrestrial level but is also in a verge to deplete the marine life, rivers. The steadinesses of the measures are being overpowered by the large amount of plastic waste (Geyer et al. 2017). Most of the wastes are being collected from the source of packaging. Therefore, it is very much essential to implement proper regulations regarding its disposal that would not affect the environment and on the other hand would find some alternatives to such problems. The innovations of social-ecological systems might be an appropriate approach to overcome such problems (Sattlegger et al. 2020).

11.9 Conclusion and Future Trends

Packaging being an essential part of the food system plays a very chief role in maintaining the quality and also enhances the marketing possibility of the product. Therefore, in order to reach the consumer’s demand, not only the organoleptic and the nutritive quality of the product should be checked, but also the packaging of the product must be given equal importance in order to gain the consumer’s attention. Therefore, proper packaging protocols should be maintained. Along with the packaging, proper packaging waste disposal should also be taken care. The increasing environmental issues due to the packaging waste disposal are the biggest concerns that are needed to be resolved through legal procedures. The problems may not be solved by only the process of recycling or proper waste management, it might also require the production of more and more bio-based materials for the packaging purpose. Biodegradable packaging materials could be an alternative to the single-use plastic packaging materials. The raw materials of such type of packaging are mostly originated from agricultural resources that are renewable. These packaging materials are environmental friendly and are a better option for the countries that use landfill for managing the waste disposal. FSSAI should collaborate with different organizations working on waste management to resolve such types of challenges and also strictly implement and execute proper rules for disposing of the non-biodegradable packaging materials (Petersen et al. 1999).

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