Chapter 11

Food Packaging: Surface Engineering and Commercialization

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11.1 INTRODUCTION

Taking research from laboratory to market is a formidable task and often the challenges met limit product innovation (the delivery of a science or technology to the market). To this end, the primary challenges lay around development of a technologically and economically viable solution that is consistent with consumer demands. The developmental work involves:

(a) understanding of technology, understanding the application area(s) for that technology
(b) proving the effectiveness of the product based on the developed technology to investors, manufacturers, customers, and any regulatory bodies
(c) developing practical methods that facilitate scaling the technology and associated production processes for large volume manufacturing
(d) consideration of costs (both production and capital)
(e) consideration of social impacts and benefits the technology will have
(f) and, finally, but most critically, the economic benefits from the technology/application

The magnitude of these challenges is such that, despite the exhaustive research work happening around the world in, for example, AM food packaging, only a small percentage of the proposed technologies bridge the laboratory to market chasm. In AM applications, a major hurdle for this has been the adequate demonstration of efficacy in real conditions that would convince stakeholders sufficiently to make the investments required to bring those AM technologies to market. This chapter is dedicated to AM food packaging technology developments in recent years especially those based on the surface engineering of polymers.

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Food wastage is a significant cost to industry and wider society and impacts all stages of the food supply chain from agricultural production, processing, storage, and transport to shelf life and end consumer use. According to the UN's Food and Agriculture Organization (FAO) approximately one-third or over 1.3 billion metric tons of all edible food produced for human consumption is lost or wasted annually throughout the supply chain due to poor practice in harvesting, storage, and transport, as well as market and consumer wastage [1]. Food loss and waste have significant negative food security, economic, and environmental impacts. The value of annual food loss and waste at the global level is estimated at USD 1 trillion [2]. Food loss and waste may decrease food availability in the market, which may in turn increase food prices and reduce the capacity of low-income consumers to access food. The resource-intensive nature of producing, processing, packaging, transporting, and storing foods mean the wasted food is a highly significant cost. The resources used to produce food that is eventually lost or wasted account for approximately 4.4 gigatonnes of greenhouse gas emissions (CO_2 equivalent) annually, making food loss and waste the world's third largest emitter, after only China and the United States [3]. It has been reported that a 60% reduction in the food wastage can reduce an estimated 84.3 million tonnes of carbon emissions every year [4]. Therefore even small extensions of food shelf life by 2 or 3 days could save billions of Euros and help build a more sustainable food industry. Lowering levels of food wastage can also impact global food security issues ensuring that future food requirements are partially met despite population growth [5]. The food packaging is envisaged to address and support sustainable development of food industry in three aspects, that is, people (social), profit (economy), and planet (environment) [6,7]. A good package should be cost efficient and provide value to generate revenue; should have a good user interface (handleability, information, etc.) and should use fewer resources, both raw materials and energy; and should be recoverable and prevent its contents from becoming spoiled.

Public health is also a critical issue. According to the two recent reports produced jointly by the European Food Safety Authority (EFSA) and the European Centre for Disease Prevention and Control (ECDC), the number of human cases of *Listeriosis* and *Campylobacteriosis* infections across 32 European countries rose in 2014, continuing a trend shown every year since 2008, along with a slight increase in the *Salmonella* cases for the first time since 2008 [8,9]. The report also highlighted the need for taking measures to reduce cross-contamination, spoilage, and on taking basic hygiene practices throughout the food supply chain.

Food spoilage occurs mainly due to (1) biochemical reactions occurring in the food leading it to degrade its color, smell, and taste and (2) microbial proliferation above acceptable limits [10–12]. The biochemical reactions largely derive from the presence of excess oxygen or moisture in the packaging or its permeation through the packaging material, for example, by oxidation of the pigment myoglobin in meat to oxymyoglobin and metmyoglobin that can be identified from the brown coloration of meat. In the second case, the microbes already present in meat and meat products can grow beyond its acceptable limit on storing it for longer time. Food contamination and recontamination can also occur during slaughtering, processing, and packaging that can subsequently grow further and spoil the food. Though conventional food preservation techniques such as refrigeration, drying, heating, and fermentation are somewhat effective in decreasing the rate of microorganism growth, these have limited value in extension of the shelf life of minimally processed high value commodities such as meat products. The nonpackaged or not properly packaged food stored by these techniques can still undergo degradable reactions through recontamination or by reaction with oxygen. Air (20% oxygen) can permeate through the package or directly react with the nonpackaged meat or meat products. The oxidation causes meat to change its color, taste, and organoleptic properties and rancidity of fats resulting in off-odor. The microbes present or contaminated may (1) attack the protein in meat causing off-odors and slime, (2) breakdown carbohydrate compounds of processed meats resulting in intense sour taste or acidity, and (3) attack the fats producing rancidity (production of lactic acid) [13,14]. All these reactions can cause to waste. Meat spoilage is, however, not a safety issue and the level of spoilage microorganisms is not an indicator of the presence of pathogens. However, it means that the meat is not of the quality that the consumer expects and may be unfit for consumption.

Development of new technologies, especially those based on nanotechnology and surface engineering, offers great promise in revolutionizing the food packaging sector [15]. As discussed earlier, opening up of distant global markets, changing lifestyles, and consumer dynamics underline the need for producing minimally processed convenience foods that are safe for consumption over a long storage period. Food packaging is a vital component in bringing produce to the consumer in a "fresh" state and that is safe. AMs are a vital part of the strategy to decrease waste and maintain health, that is, AM packaging is one potential technology that could significantly decrease food decomposition and add value for producers by prolonging product shelf life. The shelf life of a food product is defined as the period during which the product maintains its microbiological safety and organoleptic qualities at a specific storage temperature [16]. It is based on identified hazards for the product in question, heat or other preservation treatments, packaging method, and other hurdles or inhibiting factors that may be used. The shelf life can be extended, theoretically, by introducing AM functionalities and enhanced barrier properties into the packaging material. While the AM agents in a packaging system works to prevent the growth of microbes by extending the lag phase of them or by killing them [17], the high barrier films can decrease the rate of foods by the activity of gases or moisture [18].

Several strategies have been devised to exert a positive action over the packaged foodstuff, including retention of desirable molecules (i.e., aldehydes, oxygen) or release of substances (i.e., carbon dioxide, aromas). The growth of microorganisms on muscle-based food products largely occurs postprocessing and primarily during storage, therefore the packaging of such food products is paramount among all possible processing technologies in terms of delivering longer product storage stability and shelf life [10,19]. Additionally, postprocess contamination of muscle-based food products renders such products quite dangerous if contaminated with microbes of public health significance, therefore control of such microbes in longer shelf life product packs is critically important.

11.2 THE ROLE(S) OF PACKAGING

The conventional role of packaging has been the containment and protection of food from heat, light, moisture, oxygen, microorganisms, environment, and dirt. Packaging also played key roles in food preservation and protection against handling and transporting damage. The fundamental aspects of all packaging materials are that in an economic manner, they must contain, protect, preserve, inform (throughout the entire distribution process from point of manufacture to points of consumer usage), and provide convenience (at many different levels) while acknowledging the constraints placed upon their usage from both legal and environmental perspectives. As these fundamental principles apply to all forms of packaging materials and systems, it follows that irrespective of the specific level at which the packaging is industrially applied (primary sales packaging, secondary collation, and handling packaging or tertiary transport packaging), all must conform to these same principles [20]. Packaging materials used for packaging food products must conform to the fundamental principles outlined previously and satisfy all that is required of the product from both technical (containment, protection, and preservation) and sales (cost, convenience, sales information, labeling information, legal requirements, environmental requirements) perspectives [7].

The opening up of distant global markets; the advancement of technologies and societies' knowledge; and the concern about where and how food is processed, transported, and delivered, in combination with dynamic changes in the consumer preferences toward minimally processed fresh, convenience foods as well as the sustainability concern in terms of the wasted food, processes, and packaging set the platform for developing new technologies in the past decade for extending the shelf life of foods by adding components into the food packaging technology. These components are aimed at controlling bacterial, enzymatic, and biochemical reactions within the packaging via a number of strategies such as controlled release of chemicals (carbon dioxide, chlorine dioxide, sulfur dioxide, ethylene, etc.), oxygen removal, and packaging atmosphere control [13,21–26].

Currently, in case of packaged foods, the prime importance is placed to the product; its freshness, quality, and safety. Second is the esthetics of the packaging. The customer should be able to see and appreciate the food product in its packaged form. For example, for red meat products the cherry red color in a transparent well-presented packaging gets the appreciation of the customer. The quality of the product depends on how and where the food is processed, packaged, and on the packaging material and the modified atmospheric properties inside the packaging. Barrier properties, permeability, environment conditioning (gas/moisture/ethylene scavenging or releasing), and AM properties are the important requisites of packaging to keep the contained food fresh, safe, and with high quality. Along with it, the presentation of the package including its esthetics and labeling can influence the decision making of the consumer. The personality of the packaging hence is important in generating business. Intelligent packaging is one technology that has gathered momentum in recent years. The communication this functionality makes to the consumer and relevant parties make it very appealing as they would give clues to the consumer about the state of the product inside.

In a broader sense, the critical factors that the current food packaging needs to address are container integrity (prevention of damage of food by handling and transport, ability of the container to withstand its environment), security, trace and tractability of the container, AM capability, and the ability of the container material to absorb/emit or permeate gases. Food damage can occur during mechanical holding of the product or transport; the heating or cooling cycles of the product; and by contamination by microbes, such as bacteria, fungi, algae, mold, and human interaction. Mechanical, optical, barrier, antioxidant, and antimicrobial properties are the most relevant properties required for food packaging materials in order to preserve food quality [27].

Microbial contamination is a serious issue faced by the food industry even causing deaths of consumers. According to the European Food Safety

Authority a total of 5648 foodborne outbreaks were reported in the European Union in 2011. This involved 69,553 human cases, 7125 hospitalizations, and 93 deaths [28]. Most of the reported outbreaks were caused by *Salmonella*, bacterial toxins, *Campylobacter*, and viruses. The resultant current increase in consumer desire for natural, fresh, and safe products necessitates efficient food preservation from microbial contamination [29–31]. Among the known methods to incorporate AM functionality to the packaging such as through coextrusion and surface deposition, surface engineering-enabled deposition is attaining great interest due to its fast reaction time and ability to kill the microbes by direct contact AM surfaces and with their multifold actions [32]. The increasing concern of microbes attaining AM resistance makes it an absolute necessity for the AMs in the packaging to kill the microbes in different ways than a single mechanism to prevent the microbes realizing resistance against the substance. This can be achieved by either exploiting synergistic effects of >1 AM components or by using 1 AM material that displays multiple activity. In case of the natural AMs the temporal degradation of them due to their complex and continued interaction with the food matrix can reduce the AM activity over time [33]. Their restricted mechanism (single mode of action) of AM action may also be one reason that makes researchers exploring other options that led to a large number of current research focus dedicated into inorganic-based AMs, especially on silver-based formulations.

11.3 ROADMAP OF PACKAGING TECHNOLOGY DEVELOPMENT FROM THE BEGINNING TO TILL DATE

Food safety and security became the forefront of topics after the 2001 World Trade Center tragedy [34], especially concerns over possible bioterrorism through foods and water hazard begun. This, compounded with the foodborne bacterial outbreaks, has driven researchers and food industries to come up with innovative technologies that combat microbes by killing or slowing down their lag phase and thus keeping the food safe for extended time periods. The application of such AM active packaging has been performed by different methods such as by direct incorporation of AM component in foods, by coating the food product by a layer of biodegradable AM film [35], or by incorporating the AM component(s) in or on the plastic [36] used for wrapping the food product. The efficiency of AM components in the first two cases, however, is limited due to the excessive neutralization of them by the complex chemicals in food [37]. In comparison, the controlled supply of AM components from the plastic wrapping to the food makes the third type of packaging comparatively efficient [37].

Looking back at the development of plastic packaging technology, one can see a constant and continuous development and evolution of technology. The drivers for this development were the ever-increasing foodborne illness issues, the growing microbial resistance, the recognized possibilities of bioterrorism, and the ever-changing need of the dynamic consumer society for a variety of fresh and minimally processed convenience foods. The plastic packaging started with an accidental invention of a Dow Chemical lab worker, Ralph Wiley in 1933 [38]. He made a new plastic at that time—polyvinylidene chloride. This, owing to its easy "clingingness," has been used first to protect military equipment and later for food packaging applications. This product was known as Saran and has been used for protecting and maintaining freshness of food at home [38]. In 1946, Earl Silas Tupper developed Tupperware, a line of polyethylene food containers with an airtight seal that has become one of the most notable products in plastic packaging history [39]. In 1954, Robert W. Vergobbi patented zipper storage bags and in 1968 Ziploc bags were introduced as food storage bags [40]. They also introduced the first baggies and sandwich bags on a roll. In 1996, salad-in-a-bag packaging (metallocene-catalyzed polyolefins) was introduced, helping to reduce food waste and making it easier to purchase fresh produce [40]. In 2000, flexible plastic tubes were introduced, making it possible to enjoy yogurt, athletic supplements, and similar fluid foods while moving [40]. Again in 2000, a bio-based packaging, polylactic acid (PLA) made from corn was introduced to the packaging market [40].

Of course, the use of polymer materials does raise questions on the sustainability of food packaging. Across the sector, there are continued efforts to introduce ecologically compatible materials. Recycling is an important element of ecological best practice and it should be noted that this has been subject to constant improvements. The recycling rates as achieved in 2008 are plastic bottles achieving a 27% recycling rate, reclaiming 1.09 billion kg of plastic. In particular, polyethylene plastic bags and wraps achieved a 13% recycling rate, reclaiming 377 million kg of plastic. It is to be noted that the recycling rate for polyethylene plastic bags and wraps has doubled since 2005 [41].

Polymeric compounds, owing to their many beneficial characteristics, are important materials. They have high durability, high ductility, and good tensile strength and are used for manufacturing the major share of current packaging materials. Different types and forms of plastics such as polyethylenes, polypropylenes, polyvinyl acetates, polyvinyl alcohols, polyvinyl chlorides, polyethylene terephthalates, polyamides, and so on, are the primary polymers used in plastic and laminate manufacture in the packaging industry [42] for food usage. Of all the plastics available on the market for food usage, low-density polyethylene (LDPE) is the most widely used plastic in food packaging applications owing to its many advantages, such as low cost, ease of processing and forming, optical properties (transparency, color), water impermeability, but especially, because of its low processing temperature and heat-sealing ability. It is because of these latter properties that LDPE is predominantly used as the food contact plastic layer in most plastic-based laminated structures used for fresh and processed meat products. Other commonly used plastic materials in food packaging, especially for meat packaging, are polypropylene (PP) and polyethylene terephthalate (PET). These polymers are used for making trays for containing meats with or without soak/drip pads to control the juice dripping from the product. Intense research on bio-based films is also going on for developing sustainable food packaging solutions [43].

Overwraps on trays, vacuum packaging, and skin packaging are the current methods adopted for packaging meat-based food commodities. Any improvements on packaging in order to introduce AM properties or induce superior material properties (mechanical properties, barrier properties) should therefore be based on the integration of functionalities on the above-mentioned materials (mainly LDPE, PP, and PET, as well as bio-based films). Recent progress in the areas of nanotechnology and surface engineering concepts offers great promise and now enable food technologists to design novel functional nanomaterials (AM), nanocomplexes, and composites and integrate them in these polymer systems, either through incorporation into host matrices or onto their surfaces by utilizing processes, such as polymer blending, micro-perforation, coextrusion, lamination, solvent casting, or coating [44,45]. By selecting the required active/passive functionalities and processes, new packaging systems with superior properties have been attempted. The dependence of product innovation on packaging technologies makes such technologies highly desirable. Furthermore, the ever-increasing demands for more diverse high-quality consumer food products, including that of muscle-based food products, underline the need for feasible and cost-effective innovative packaging technologies [46].

A great amount of research has been dedicated to develop new solutions and products based on active and intelligent packaging to meet adequate safety requirements. Many of the products have shown efficiency in in vitro tests and a portion of these have also proven effective in in vivo trials. However, the commercialization of these technologies is limited and only a few could reach the marketplace, primarily due to reasons such as strict safety and hygiene regulations, limited consumer acceptance, and high cost. The present negative concept on additives, especially nanomaterial-based additives, in or on packaging materials is considered as almost unacceptable by the consumers [47,48]. Developing consumer awareness as well as clarifying doubts/concerns among the consumer society regarding the negative/positive impact of any technology is therefore another hurdle in the commercialization of many nanomaterial-based food packaging technologies. Further, the strict regulations imposed by agencies like Food and Drug Administration (FDA) and Environmental Protection Agency (EPA) mean that novel food packaging technologies will take longer times for commercialization.

The most successful and widely accepted AM technology for meat products is the AMs incorporated in pads and kept underneath the food in the packaging tray [10,11,19,49,50]. This, in combination with modified atmospheric packaging (MAP) technologies, is currently used to extend the shelf life of meat products. The use of AMs in sachets is another technology employed for a wide range of food commodities. The AMs mainly used in these technologies are carbon dioxide, chlorine dioxide, sulfur dioxide, ethanol, organic acids, essential oils, and silver ions. Volatile gas-based technologies are based on the release of the vapors into the headspace of the package, thereby, coming in contact with the food product and helping to reduce microbial growth [23,27].

Technologies based on incorporation of AMs in the polymer matrix mainly by coextrusion have shown some commercial success in terms of shelf life extension. Silver ion-based AM packaging is the most successful commercial products in this section and is discussed further later. The AM action of these is mostly relied on the migration of the ions into the surface of the packaging and subsequently on to the food product, thereby, inhibiting the growth of microbes [51,52].

From a recent survey by the Centre for Food Safety, it has been found that >60 foods and food contact products containing nanosilver are commercially available cutting edge the United States. The survey by European Food Safety Agency has found that >120 nanosilver food applications have been commercialized around the world [53]. Silver-based food contact materials/products have mainly been commercialized in countries such as the United States, Germany, Korea, and China [54]. They include mug cups and baby milk bottles (Baby Dream Co. Ltd., Korea), frying pans (Queen-Art Co. Ltd., Korea, Westfalia Wergzeug Company GmbH & CO KG, Germany), cutting boards (A-DO Global, Fine Polymer, Inc., New Life Co. Ltd., Korea; Pro-Idee GmbH & Co. KG, Germany), and food storage containers (A-DO Global, Fine Polymer, Inc., Korea; Blue Moon Goods, LLC, Sharper Image, United States). Various silver formulations have also been used as supplement drinks especially in the United States (MaatShop, American Biotech Labs, Greenwood Consumer Products, Natural Care

Products, Purest Colloids Inc., RBC Life Sciences Inc., Utopia Silver Supplements, Natural Immunogenics Corp. and Silver Lozenges and other products by Activz) but also in Germany (FairVital), Korea (Natural Korea Ltd., Phoenix P.D.E. Co Ltd.), and in New Zealand (Skybright Natural Health).

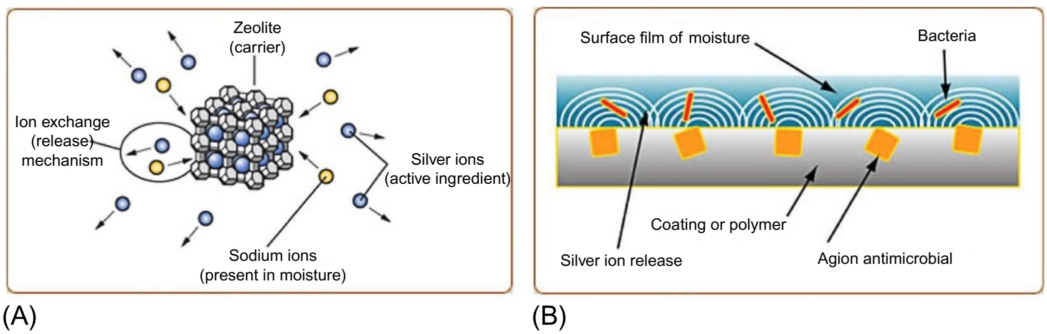
The incorporation of natural AMs though has been tried and tested has shown limited commercial success due to their high process time loss owing to their lower temperature stability [36,55]. Another type of commercial packaging materials that are available are certain biodegradable polymers such as chitosan, poly-L-lysine, poly(lactic acid) (PLA), and alginate films [43,56,57]. The interaction of charged amines of the polymers (chitosan and poly-L-lysine) with negative charges of the microorganism cell membranes is shown to lead to their leakage and eventual cell breakage [58]. Films made of PLA are mainly used for packaging such as cups, bowls, bottles, and straws, as well as disposable bags, trash liners, and compostable agriculture films. Though they have good mechanical strength, chemical resistance (to hydrocarbons, vegetable oils, etc.), and low oxygen and CO_2 transmission rates, their commercial application is currently limited due to their high moisture vapor transmission.

11.4 BULK VS SURFACE ENGINEERING OF PACKAGING MATERIALS (TECHNOLOGY)

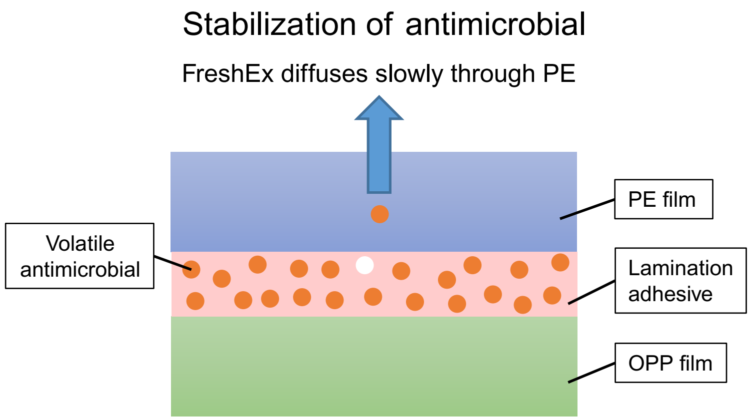
Most of the commercialized technologies around incorporated antimicrobial functionality in food packaging have been through bulk engineering, that is, inclusion of antimicrobials into the bulk of the polymer [59]. Of those technologies, nanoclay-based formulations form the majority of materials [24]. In particular, nanoclays that have additional silver ions incorporated into them have been claimed to have comparatively (to other nanoclay-based preparations) superior activities. Considering the minimal leachability/migration of silver in these packaging materials, the extended shelf life is considered to be a result of the combination of properties. These include improved mechanical and barrier properties of these films along with the antimicrobial activity. The minimal leachability of these materials is as a result of them being either in the bulk as opposed to the surface or having them incorporated in carrier material cavities. The barrier properties of these packaging materials are improved as a result of the distribution and arrangement of the layered nanoclays in the matrix as parallel plate-like inclusions, or filling of the nanoparticles in the free volumes of polymer matrix, thus creating a tortuous path for gas diffusion through the films [18,52,60]. The mechanical properties are improved by the arrangement of nanoclays in the polymer matrix where the organic molecules in them link with the polymer and arrange in a favorable manner thus improving the crystallinity of the films [61].

Agion technology by Zeomic is an inorganic AM powder-based technology approved by FDA and being used in the United States for all kinds of food packaging materials such as wrappings, bottles, films, and trays as well as resin materials used for chopping boards and belt conveyers employed in manufacturing processes [30]. The technology is based on the dispersion of the AM powder into the resins including PE, PP, PS, acrylonitrile styrene (AS), acrylonitrile butadiene styrene (ABS), polycarbonate (PC), polyoxymethylene (Acetal) (POM), polyvinyl chloride (PVC), polyethylene terephthalate (PET), polybutylene terephthalate (PBT), and polyamide. As the name indicates, the AMs (such as silver or copper ions) are incorporated into the zeolite cavities, which work as a controlled release agent, before dispersing them into the resin. According to Sciessent's customized Agion AM technology, though they are used in other applications than food packaging, the mechanism is based on an ion exchange release process [62]. When the material comes into contact with moisture, the ions exchange with the positive ions (often sodium) from the moisture, effecting a release of the AM elements "on demand" (Fig. 11.1).

In another technology by American Packaging Corporation, which is yet to be commercialized, an all-natural AM is incorporated into the lamination adhesive which then diffuses through the food contact layer into the package (Fig. 11.2) [63]. This technology seems to be currently under product and field testing.



■ **FIG. 11.1** (A) The patented multifaceted zeolite crystal carrier provides a three-dimensional release mechanism that provides efficient release of ions independent of particle orientation in the substrate, © Sciessent 2017 www.sciessent.com. (B) The ion exchange process at the surface. Zeolite crystals containing elemental ions are randomly oriented and distributed through the surface of a fiber, polymer, or coating. In conditions that support bacterial growth, positive ions, in ambient moisture, exchange with elemental ions at reversible bonding sites on the zeolite. The exchanged ions are now available to control microbial growth, © Sciessent 2017 www.sciessent.com.



■ **FIG. 11.2** Schematic showing the mechanism of AM activity of the film. An all-natural AM is incorporated into the lamination adhesive which then diffuses through the food contact layer into the package.

11.4.1 Surface Engineering Concept for the Application in Food Packaging

Recent developments show an increased focus on active food packaging concepts based on surface engineering of polymers or surface coating deposition of AM agents on film surfaces. The main advantage of this concept was the envisaged quick availability of AMs from the direct contact layer inside of the food package. This concept can be particularly useful considering the comparatively higher moisture content and other favorable atmospheric conditions at the food product surface that may facilitate AM growth. A provision for "on-demand" AM delivery by the direct contact surface was proposed to be the ideal technology to address this issue. In an attempt to compare the efficacy of AM surface coating with bulk impregnated AM, Ha et al. prepared grapefruit seed extract (GFSE) incorporated PE films by both coextrusion and a solution coating process and assessed their feasibility against the growth of microorganisms such as *Escherichia coli*, *Staphylococcus aureus*, *Bacillus subtilis*, and *Mucilaginibacter flavus* in ground beef [55]. They found that both types of AM films reduced the growth rates of bacteria on ground beef stored at 3°C, as compared with plain PE film; however, the coating resulted in a higher level of AM activity than the coextruded film. The coextruded film (15 μm thick) with 1.0% (w/w) grapefruit seed extract showed AM activity against *M. flavus* only, whereas the coated film (43 μm of LDPE with 3 μm of coating layer) with 1.0% (w/w) grapefruit seed extract showed activity against *E. coli*, *S. aureus*, and *B. subtilis*.

They prepared the GFSE coating (0.5% or 1%) with the aid of a 40% polyamide binder (Versamid 750) in 2:1 isopropanol/*n*-propanol by a spread coating method after a corona pretreatment of the LDPE substrate. Cooksey has shown the inhibitory effect of nisin coated onto LDPE film, using a cellulose-based coating method, against the growth of *S. aureus* and *Listeria monocytogenes* in a nonfood system [64].

Cerisuelo et al. has prepared carvacrol, citral, marjoram essential oil, or cinnamon bark essential oil incorporated surface coatings on PP and PET substrates by using a polyethyleneimine anchor and ethylene vinyl alcohol (EVOH) matrix [36]. They showed that a corona discharge followed by polyethyleneimine primer coating was effective in depositing AM-incorporated EVOH. They also showed the effectiveness of bentonite nanoclay in improving the physical properties of coated films on incorporation into the EVOH matrix.

AM coatings on plastic substrates were also prepared by chemical vapor deposition from alcoholic solutions of metal nitrates such as silver, copper, and zinc [65]. Another type of AM coating prepared by using zein as the binder and ethanol as carrier and a metal- or nonmetal-doped TiO_2 as the active materials was patented [66]. Schroeder and Scales patented charged organic molecule-based AM coatings on plastics [67]. The coating was obtained by covalently bonding quaternary ammonium and phosphonium salts onto a polymeric material.

Though a large number of studies have been reported on surface engineering and surface coating-based methods, their commercialization has been limited by the availability of silver and consequent migration (to the food) related regulatory issues. The direct contact of silver coatings (as films or nanoparticles, etc.) and the food makes these technologies somewhat less preferable by the industry and the technologies are not well developed at an industrial level. However, continued research efforts and developments are ongoing to address this shortcoming. Intensive research is focused on maximizing the antimicrobial capacity of surface-coated functionalities with a minimum possible surface concentration.

Recently, Morris, Kerry, and coworkers have demonstrated the in vitro antimicrobial potential of surface-engineered silver-based antimicrobials against Gram-positive (*S. aureus*) and Gram-negative (*Pseudomonas fluorescens*) bacteria. They have then demonstrated the in vivo antimicrobial activity of novel packaging materials developed by a surface coating technique and shown shelf life extension of skin packaged chicken breast fillets under chilled (4°C) storage conditions [68]. Their surface engineering concept was based around a block copolymer (BCP) assisted deposition of silver ions in nanocavities formed by self-assembly driven phase separation of the BCP under suitable conditions [69]. This simple technique allows direct deposition of materials and functionalities onto a range of substrates. Self-assembly is a process of self-organization of materials or components into patterns or structures without the assistance of any external forces or manipulation. BCPs are made of two or more chemically distinct polymer blocks within a single molecule. The minimum energy arrangement of blocks within the bulk or a surface film is when the component blocks are separated to their maximum extent and share their interfaces to the minimum possible extent. The presence of the covalent linkage in the middle, however, keeps the blocks still connected restricting their separation, thereby causing them to freeze within a phase-separated nanoscale structure.

11.4.2 Block Copolymers and Their Phase Separation Chemistry

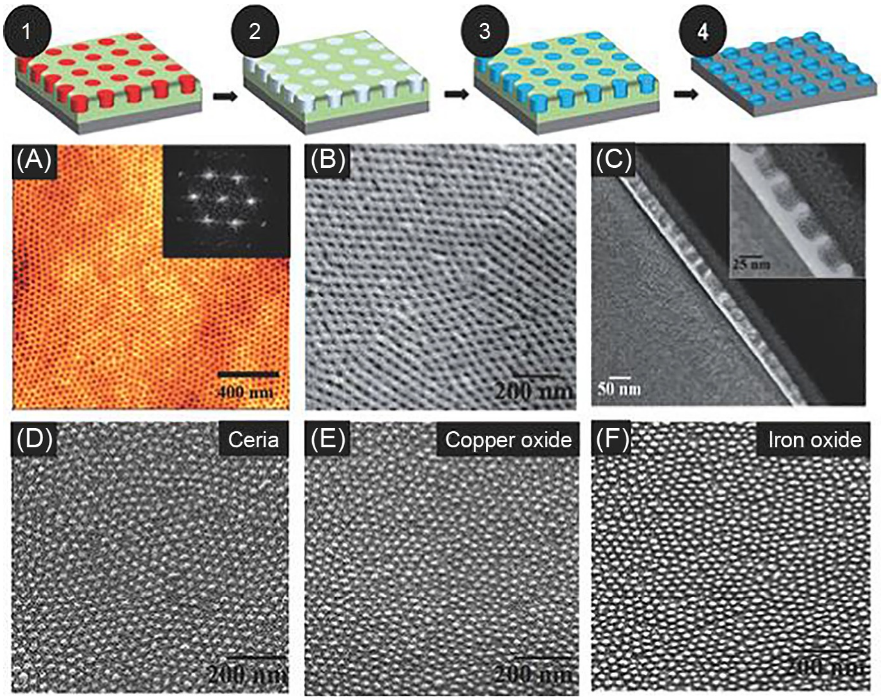
BCPs are composed of two or more chemically distinct polymeric segments that are usually immiscible with each other. Several types of BCPs have been reported to be capable of forming phase-separated nanopatterns, including PS-*b*-PEO polystyrene-*b*-polyethylene oxide, PS-*b*-PMMA (PS-*b*-polymethylmethacrylate), PS-*b*-PV2P, (PS-*b*-poly(2-vinylpyridine)), PS-*b*-P4VP, PS-*b*-PDMS (PS-poly(dimethylsiloxane)), and PS-*b*-PLA (PS-*b*-polylactic acid) [70]. The self-assembly of BCPs can be controlled by selecting BCP blocks with different molecular weight, degree of polymerization (N), and volume fraction (f), which in turn will define the strength of the interaction between the blocks (represented by the A-B Flory-Huggins interaction parameter χ). In other words, the architecture and composition (e.g., molecular weight, molar ratio) of the BCPs affect the morphologies of the self-assembled structure and form phases such as spherical, cylindrical, bicontinuous porous, or lamellar [71]. The self-assembly of BCP and current research on BCP materials impregnated with various inorganic materials have been discussed in detail previously [70,72]. One particular advantage of the BCP self-assembly process, that is applied in AM packaging, is its ability to produce a variety of structures such as spheres, lamellae, cylinders, gyroid arrangements, and so on, thereby enabling this process to be a promising method in terms of manipulating the structure and shape of nanoscale materials.

Owing to the simplicity and effectiveness of the BCP patterning technique, it was used for generating Ag nanodots on various substrates by Morris and coworkers, who demonstrated that this approach has the potential to be used as a simple method for developing AM active packaging materials. In a typical BCP-based self-assembly process, the BCP, with chemically distinct polymer blocks that are linked together by a covalent bond (e.g., PS-*b*-PEO) as used by this group, is allowed to self-assemble on a substrate at room temperature or slightly elevated temperature (<60°C) while in the presence of a suitable solvent or solvent mixture that selectively swells one (or both) of the component block(s) of the BCP [73–75]. The swelling allows free movement of the polymer chains that are generally entangled following coating. When this solvent annealing process is stopped after an optimum heating period, the blocks freeze into a phase-separated pattern. The prepared self-assembled PS-*b*-PEO pattern can be used as a template to create Ag nanodots by depositing an ethanolic solution of $AgNO_3$ onto the patterned substrate, which, on subsequent drying and curing, will be attached to the BCP pattern. The schematic of the methodology that can be used for AM deposition on the surface of the polymer is illustrated in Fig. 11.3. The BCP coated onto a substrate surface was microphase separated by an annealing process into a cylindrical pattern (a), the active AM Ag was subsequently incorporated onto the nanocylinders by spin, dip, or spray coating and a low temperature heating process (<60°C) produced an intact Ag-coated surface (b). Such self-assembled PS-*b*-PEO or any other suitable BCP pattern can be used as templates to coat AM materials, from preformed NP solutions (Ag/Ag_2O, Cu/CuO, TiO_2, ZnO, MgO and a host of naturally occurring AMs) or their precursor salt solution [76].

11.5 COSTS AND PRACTICALITIES

In almost all of the film-based food packaging technologies, the film manufacture is based on hot blowing, extrusion, or coextrusion. The required mechanical and other properties of films are then defined by laminating different layers with appropriate properties [77]. These multilayered packaging materials are specifically designed to enhance the long-term preservation of food products. However, such developments in packaging have reduced the recyclability of materials as the multilayers are difficult to separate in any recycling process. The less recyclable products are therefore shredded and reextruded into plastic pellets and/or they are relegated to lower value uses such as plastic lumber for park benches rather than new packages [78]. This process called cascaded recycling can only slightly reduce the burden on plastic wastes.

The environmental cost of packaging is a serious concern. A study by Trucost, a consulting group that reports the environmental impact of business practices in dollar terms, for the United Nations Environment Programme, in 2014, estimated the environmental cost of using plastics to be $75 billion



■ **FIG. 11.3** Schematic of a typical BCP patterning process and metal salt inclusion to form metal/metal oxide nanodot arrays. (1) Self-assembled PS-*b*-PEO BCP nanodot pattern following solvent vapor annealing. (2) "Activated" film formation after immersing in ethanol. (3) Metal ion inclusion via spin coating on "activated" PS-*b*-PEO nanodot template. (4) Metal oxide nanodots after inclusion and UV/O_3 to oxidize metal ions and remove the polymer matrix. (A) AFM image of microphase-separated PS-*b*-PEO film. (B,C) SEM image and TEM cross-section image of nanoporous PS matrix following "activation" using ethanol. SEM images of (D) ceria, (E) copper oxide, and (F) iron oxide nanodot arrays following metal salt inclusion process. *(Reproduced with permission from T. Ghoshal, et al., A general method for controlled nanopatterning of oxide dots: a microphase separated block copolymer platform, J. Mater. Chem. 22 (24) (2012) 12083–12089. Copyright 2012, Royal Society of Chemistry.)*

annually, where the contributions from food and soft drinks sectors were 23% and 12%, respectively [79]. These calculations were based on costs of disposal and greenhouse gas emissions. Although this is a highly significant sum it is balanced by costs associated with improper use of food packaging. The environmental cost of food waste, the cost of producing and processing of the wasted food, its negative impact on the sustainability of food industry, so on, are significantly greater than any costs associated with the packaging although this will differ with food types. High-value products such as meats gain a bigger benefit from packaging because they are more resource intensive to produce than bulk goods such as rice. A recent assessment on the overall environmental performance and the effect on food loss reduction of a food and its active packaging showed the potential of active food packaging in alleviating global warming, reduction of fossil energy demand, and also in reducing acidification potential and eutrophication impacts [80]. Indeed, the packaging % cost as compared to the total cost of the product can be considered as sustainable if the packaging can maintain the high quality of food for longer shelf time and also can connect with the consumer with its esthetics, personality, and labeling-enabled communication.

The challenges of novel packaging technology developments and packaging material manufacturing are mainly based around the processing cost. These costs can be associated with materials or with capital investments that might be required to develop the process. The acceptance and uptake of a lab-proven technology depends hugely on its ability to integrate into the existing manufacturing setups and machinery. Adding additional steps to an overall packaging material manufacturing process to the existing manufacturing process can add significant equipment requirements and any additional steps need to be consistent with production rates and not decrease output through a production cycle. If this is not practical and is costly (compared by market requirements) than any process developed it will not be acceptable to industry. However, the increase in cost can be considered as sustainable if the packaging material can offer sufficiently extended shelf life for products so that profitability can be maintained or improved. Therefore the main challenge for novel antimicrobial concepts is to address this additional step cost in terms of their improved shelf life feature.

Printing and dip coating are two potential process steps that could be integrated to the existing film manufacturing setup for producing surface-engineered films. However, the success of these technologies and processes will ultimately depend on the cost-benefit ratio. One of the major hurdles in the commercialization of food packaging technologies, especially surface engineering technologies, is therefore the process cost. Conventionally, flexo or gravure printing is used by a vast majority of packaging companies. Typically, the printed film production speeds are 100–400 m/min. If one wants to scale-up a dip- or spray-based process, the residence time of the process could be higher than the conventional process. This is because the film role has to go through processes such as dip/spray, solvent removal, heating, and so on. Assuming if the residence time of the process is 2–5 min, if the speed is $\sim$1 m^2/min, then it will produce 12–30 m^2/h. If minimum wage is considered as 10 €/h, it becomes 0.33 to 0.83 €/m^2. Companies consider such processes as prohibitively expensive. Food packaging products that increase the cost by 0.02 €/m^2 fail to launch.

According to a new market report published by Persistence Market Research, the global nano-enabled packaging market for food and beverages industry was worth USD 6.5 billion in 2013 and is expected to grow at a CAGR of 12.7% during 2014 to 2020, to reach an estimated value of

USD 15.0 billion in 2020 [81]. Active packaging is a significant contributor to this growth. However, the experts still believe that nanotechnology is at a nascent stage, especially its usage in food packaging is low as compared to other industries. Though there are a number of companies providing nano-enabled packaging solutions to the food and beverages industry, limited numbers of buyers have shown interest to negotiate with nanotechnology companies. The consumer's preferences for natural food products have been the primary inhibiting factor for the implementation of emergent nano-food packaging technologies. However, further development of such technologies and risk assessment-based proofs may be able to address consumer concerns enabling further development of AM active food packaging market.

11.6 RISKS AND BENEFITS

Plastic packaging materials can be harmful if adequate measures for chemical leaching are not taken. All plastic packaging materials are made from chemicals that have the potential to harm a person's health. The chemicals that make up plastics include harmful industrial chemicals such as bisphenol A (BPA) and diethylhydroxylamine (DEHA). However, their leachability into the food is limited as defined by appropriate quantity regulation. When AM active materials are incorporated, the possibility of their migration into the food product is a significant issue. This is especially for materials for which the basis of antimicrobial degradation or inhibition is migration. Thus it has to be ensured that the migration is limited below the allowed regulatory limit but also allowing the active materials to exhibit the activity required to extend the shelf life of the product. The use of nanomaterials can be considered to be problematical for end users. Although nanomaterials are simply the nano-sized analogs of materials in their bulk or higher dimensional state, very often their potential to impact human health is unknown. Nanomaterials, due to their very small sizes (<100 nm) and high surface-to-volume ratio usually show dramatic changes/improvements in their optical, electrical, electronic, and functional properties as compared to their bulk analogs and, thus issues such as nanotoxicology are difficult to predict. However, in general, nanomaterials are shown to cross biological membranes and access cells, tissues, and organs. Nanomaterials are also shown to catalyze the production of reactive oxygen species [82]. In one of the nanotoxicology studies of nanosilver, the exposure of AgNPs was correlated to a significant increase in mitochondrion indicating the possibility of genetic fragmentation [83]. Compared to larger size particles, their handling during material preparation can be an additional concern since they are highly air borne. Therefore rigorous safety measures need to be taken in industrial production units involving nanomaterials. However, studies have shown that the harmful effects of nanomaterials entering through skin are less as compared to them entering by ingestion or by breathing [84]. These studies are however not conclusive [85,86].

Surface-engineered AMs have their own potential risks and benefits. The risks are mainly based around their migration into food and ultimately into the human body. Further, the hazardous chemicals and surfactants usually used for defining their size and shape in the process can also pose threats to humans [87]. However, if AM nanomaterials are incorporated on the surface of films such that they are slowly released over a period of time can effectively address spoilage and pathogenic microbial contamination thus ultimately increasing the shelf life of food products. The technology developed by Morris, Kerry, and coworkers is unique in that the AMs are incorporated in nanocavities formed from BCP pattern, which can be in direct contact with food products and so readily available to the food surface but in a controllable manner. This could mitigate the growth and proliferation of microbes on food surfaces as they have demonstrated against model Gram-positive (*S. aureus*) and Gram-negative (*P. fluorescens*) bacteria [69].

In general, the benefits of packaging include the possibility of feeding more people (in extended markets) with high quality food (if the shelf life can be extended), but involving processes and materials that involve less environmental pollution and lower carbon emissions achievable as a result of reduction of food waste, better food safety, food security, and the prospect of sustainable food development. The benefit of surface-engineered AM technologies is their faster action toward the most vulnerable microbial growth sites (surfaces) making it a powerful food safety and security tool. Silver-based surface engineering technologies are promising in this regard, as they are proven wide spectrum AMs. AgNPs are reported to have shown comparable and even better bactericidal properties than penicillin against microbes such as *E. coli* and *S. aureus* [88]. However, the use of silver in food products is strictly regulated by the FDA and EFSA. Currently, the allowable limit of silver ions that can be leached into the food is limited to a maximum of 0.05 mg/kg of food [89]. Silver (E 174) in the form of silver zeolite is authorized as a food additive in the European Union (EU) in accordance with Annex II to Regulation (EC) No 1333/2008 and (EU) No 231/2012 based on the human no-observed-adverse-effect level (NOAEL) of about 10 g/kg silver for a total lifetime oral intake for drinking water [89,90]. The challenge for the researchers here is in developing technologies that are effective in microbial mitigation, using AM agents that are migrated into the food below their regulated limits. The neutralization of AM's activity by the complex proteins and chemicals in meat products adds further complexity to this already significant challenge. The exploitation of AM and antioxidant activity of natural antimicrobials is another possibility by which the shelf life can be extended using surface engineering techniques [91]. However, the retention of organoleptic properties of food is a serious challenge when natural AMs are used. Exploitation of hurdle technologies involving the usage of inorganic and natural AMs along with modified atmospheric conditions would be one ideal route toward its commercialization [92], considering these facts. However, the commercialization of such technologies will only be possible when they have been approved after a rigorous migration-related risk assessment process and validation. Effective communication about the implications and benefits of the technology to consumers is also key in their commercialization process for better consumer acceptance and market penetration [93].

11.7 SAFETY CHALLENGES

The safety of food products against foodborne microbes, quality assurance, safety from possible bioterrorism, consumer preference, awareness, and acceptance are the key drivers of current and emerging food packaging technologies and food industry. Implementation of procedures to avoid contamination of spoilage and pathogenic bacteria at the time of food production, processing, and packaging is the primary challenge of food technologists and industry as a whole. Especially for meat and poultry products, as they could be inherently contaminated with pathogens grown in their guts, their farming also plays important role. Adequate technologies are also required for the subsequent stages, which is slaughtering and processing of the products, to reduce cross-contamination and more contamination. Bulk or surface engineering technologies therefore could also play a big role in the manufacture of cutting boards, processing vessels/equipment, food storage room furniture, and small and bulk food carrier boxes.

The increasing resistance of microbes against AMs and antibiotics is another challenge for the food packaging industry. The use of preferred natural AMs such as plant extracts and essential oils may be limited in combating the increasing AM resistance. A multimodal microbial killing platform will be more preferable in this respect. Synergistic use of AMs, hurdle technologies, and the use of silver- or copper-based AMs are proposed as potential solutions. In particular, silver-based packaging solutions are promising considering the multiple mode of action of silver ions in inhibiting the microbial growth [18]. They could attach to the microbial cell wall and break them eventually permeating and destructing them, as well as enter the cell cytoplasm and obstruct their respiration, multiplication, and enzyme activities.

In these multiple ways, they can ensure microbial growth is prevented. However, as in all the nonnatural, especially inorganic AMs, the migration of unwanted quantities of silver ions into food product is a concern which currently questions the commercialization of direct contact silver-based packaging materials.

When considering the surface-engineered AMs, the provision of them diffusing/migrating into the food surface "on demand" will be the best and practically viable technology. Applying them as coatings embedded in nanoclays has been reported [36]. The challenge here will be the compliance to regulatory requirements in terms of migration and color issues as the industry is looking for colorless transparent films for better display and consumer acceptance [94–96].

11.8 FUTURE OF PACKAGING

As we have discussed, AM active food packaging is becoming a key component in the food value chain, in particular, in the wake of opening up of new distant markets and opportunities, increasing requirement for high quality minimally processed convenience foods, food safety against possible bioterrorism, food security, sustainable food development, and increasing concerns over microbes attaining microbial resistance. In terms of commercial aspects, increasing product shelf life reduces costs such as spoilage allowance, end of code date write-downs, and increases returns. However, the commercialization of novel AM packaging technologies is slow due to several reasons such as strict safety and hygiene regulations, limited consumer acceptance on product effectiveness, and high cost.

The development of new technologies in the AM food packaging sphere, however, is promising as novel concepts and technologies are surfacing in greater frequency due to the unmet and urgent need for sustainable technologies for providing high quality safe food to the consumers. However, the cost and consumer acceptance are the key factors that will determine the commercialization potential of novel AM packaging technologies. In order to achieve a reasonable cost, the process of manufacturing AM films should be simple and integratable with the existing processes and manufacturing facilities. Further, the films should be chemically stable for long-term usage and storage.

Any commercial endeavors for implementing food packaging solutions must deal with multiple and very complex issues. These include satisfying and appealing customers, satisfying regulatory bodies, as well as to have a cost-effective, cost-competing manufacturing technology. As meat is very much an appearance-led product, the consumer acceptance is mainly based on their presentation at the retailer. It should be esthetically presented, should have right color, texture, smell, and should appear fresh to the consumer. In terms of the technology, though AM packaging concepts are promising, the multiple challenges offered by meat products mean a synergistic approach with multiple hurdles would be ideal than a single hurdle for inhibiting microbial growth and spoilage. This is because, for example, microbial growth inhibition may only be able to keep the food safe, but still there is the issue of product appearance for better consumer appeal and acceptance. Retaining good texture, water content, ideal pH conditions, and color will make the product more presentable and with good sensory properties and taste. The synergistic use of AM technologies and MAP or vacuum packaging conditions could address such multiple issues and offer a systemic solution.

When it comes to surface engineering technologies, the main challenge for them is to be consistent or compatible or integratable with the existing manufacturing processes. Any deviation, such as addition of more steps to the existing manufacturing setup, is deemed as detrimental in terms of cost aspects, as explained previously. However, as there is urgent and unmet need for shelf life-extending technologies, a robust process that offers a significant extension in shelf life (such as 3–5 days for meat products) may be able to withstand the cost concerns and be accepted by industries. From a packaging companies' perspective, when they run trials on new films at the plant they look for: (a) running of the machine without issue, (b) film clarity/transparency, and (c) shelf life the film offers. The food producers/distributors, on the other hand, look for (a) health and safety, (b) migration issues, (c) shelf life, and (d) recyclability. The commercialization of novel food packaging technologies is, however, a formidable task as, still, one company has to take the lead and start/introduce an otherwise unconventional manufacturing process, if that is different from the existing manufacturing setup. The current multimillion dollar manufacturing setups in place, high processing throughputs and demands, however, make industries play safe than going for such possibly positively disruptive changes.

When it comes to regulation, there are many hurdles for surface engineering technologies to address. They are those put down by FDA, EFSA, EPA, and so on; a systemic solution should address all these aspects and should be competent in cost aspects as well. The authors believe the current developments in food packaging research toward the realization of this goal are looking very promising and in the right direction to help a sustainable development of the agri-food sector.

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