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Review

Active Agents Incorporated in Polymeric Substrates to Enhance Antibacterial and Antioxidant Properties in Food Packaging Applications

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Abstract: Active packaging has played a significant role in consumers' health and green environment over the years. Synthetic polymers, such as poly(ethylene terephthalate) (PET), polyethylene (PE), polypropylene (PP), polystyrene, poly(vinyl chloride) (PVC), polycarbonate (PC), poly(lactic acid) (PLA), etc., and naturally derived ones, such as cellulose, starch, chitosan, etc., are extensively used as packaging materials due to their broad range of desired properties (transparence, processability, gas barrier properties, mechanical strength, etc.). In recent years, the food packaging field has been challenged to deliver food products free from microbes that cause health hazards. However, most of the used polymers lack such properties. Owing to this, active agents such as antimicrobial agents and antioxidants have been broadly used as potential additives in food packaging substrates, to increase the shelf life, the quality and the safety of food products. Both synthetic active agents, such as Ag, Cu, ZnO, TiO_2, nanoclays, and natural active agents, such as essential oils, catechin, curcumin, tannin, gallic acid, etc., exhibit a broad spectrum of antimicrobial and antioxidant effects, while restricting the growth of harmful microbes. Various bulk processing techniques have been developed over the years to produce appropriate food packaging products and to add active agents on polymer matrices or on their surface. Among these techniques, extrusion molding is the most used method for mass production of food packaging with incorporated active agents into polymer substrates, while injection molding, thermoforming, blow molding, electrospinning, etc., are used to a lower extent. This review intends to study the antimicrobial and antioxidant effects of various active agents incorporated into polymeric substrates and their bulk processing technologies involved in the field of food packaging.

Keywords: food packaging; active agents; bulk preparation techniques; antibacterial and antioxidant properties

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1. Introduction

Food packaging is an integral component of the food processing industry that aims at achieving the safe transportation and distribution of the products in wholesome conditions to the consumers. Currently, polymers play a significant role in the manufacture of packaging materials due to their desirable properties including resilience, stability, and ease in production. Nevertheless, the increased usage of plastics has caused serious environmental issues because of their resistance to biodegradation. Biopolymers on the other hand are a sustainable solution to the issues posed by plastics as they easily degrade in the environment and imitate the properties of traditional polymeric materials. [1]. However, a significant problem in the food packaging sector remains a challenge. Microbial spoilage threatens numerous food products such as meats, cheeses, baked products, poultry, fruits, and vegetables [2], leading to an increased demand for antimicrobial-based food packaging materials during the 21st century. Hence, various techniques have evolved in the food packaging industry to extend the shelf life of foods and provide germ-free foods to consumers. For that reason, various active agents have been incorporated into the polymeric substrates to improve their mechanical, barrier, antioxidant, and anti-microbial properties. "Antimicrobial agents" have been widely used to disinfect the microorganisms present on packaging surfaces, in households, on personal protective equipment, etc. At the same time, food packaging industries have also been focused on reducing the environmental impact caused during the disposal of packaging products, with green packaging playing a crucial role in the waste disposal system [3,4].

Active agents have been extensively incorporated into both synthetic and biobased polymers to improve the shelf life and food quality. Specifically, nanoparticles have been facilitated onto a large scale as active agents in modern packaging to produce nanocomposites, and nano-based sensors able to detect changes in food products [5]. However, active agents for packaging must be carefully selected based on their activity against targeted microorganisms and their sustainability after incorporation into the packaging substrate [6]. According to the European Commission's regulation regarding the active and intelligent materials intended to come into contact with food, a maximum of 0.01 mg/kg migration of nonauthorized substances through a functional barrier is acceptable in food packaging. This regulation was proposed after considering infants and other particularly susceptible persons [7]. The effect of the active agents also depends on their release kinetics. If the release rate of an antimicrobial agent is high enough, the food spoilage could be inhibited before it even starts. A Fickian diffusion model and non-Fickian diffusion model are the two most commonly used mathematical models to determine the release profiles [8–10]. The degradation rate of polymer composite materials depends on the nature of the materials, how strongly the fillers and matrix are bonded to each other, and the environmental conditions, such as temperature, moisture, pH of soil, microbial population, and nutrient supply [11]. The area and properties of the exposed to environmental interface plays an important role in the degradation of polymer composites. A composite with a rough surface and polar hydrophilic functional groups tends to have a faster biodegradation than a smooth, hydrophobic, and inert one [12]. Most of the natural active agents are hydrophilic in nature and tend to provide a good adhesion to the surface of the composite materials and microorganisms in the environment, which favors biofouling [13]. The active agents must meet certain requirements when used as coatings: they should adhere well to the coating surface, the concentration of release agents, and the equivalence of properties provided by the conventional passive packaging [14].

Currently, synthetic antimicrobial active agents are widely used in the field of food packaging. The most well-known "antimicrobial agents" and antioxidant active agents in food packaging are organic acids, such as benzoic acid, propionic acid, and their salts, inorganic metallic ions, such as silver ions and titanium ions, natural compounds, such as bacteriocins and lysozyme, and plant extracts, such as essential oils, allyl isothiocyanate (AIT), etc. Moreover, synthetic antioxidant agents such as butylated hydroxytoluene (BHT), butylated hydroxyanisole (BHA), and tert-butylhydroquinone have been phased out and replaced by natural antioxidants, such as chitosan, alginate, gelatin, galactomannans, and cellulose derivatives. When it comes to commercialized antimicrobial active agents, there are only few available due to the strict hygienic regulations concerning food packaging in different countries. Several of the commercially available products on the market, such as silver (Ag)-substituted zeolite or zirconium used in poly(vinyl chloride) (PVC), linear low-density polyethylene (LLDPE), polyethylene (PE), rubber matrix for wrap films, etc., are sold under the trade name Agion® (Wakefield, MA, United States), Zeomic™ (Nagoya, Japan), and Cleanaid™ (Cardiff, United Kingdom). Chlorin dioxides used in the polyolefin matrix for packaging films are sold under the trade name MicroGrade™ (Barnet, United Kingdom), Knick'n'clean® (Hannover, Germany). Triclosan used in polymers, rubber, etc., and used in sheets or pads is sold under the trade name Uvasy™. Wasabi (Cape Town, South Africa) (Japanese horseradish) extract encapsulated in cyclodextrin used in coated poly(ethylene terephthalate) (PET) films is commercially available under the trade name Wasapower (Tokyo, Japan) [15,16].

Polymer processing technologies are used in the mass production of products with various colors, designs, and complicated shapes to meet the long-life applications for use in industries such as food packaging industries to produce cling films, laminated pouches, plastic wraps, bubble warps, plastic containers, tins, cans, tetra packs, laminated tubes, etc. Generally, petrochemical-based plastics, such as poly(ethylene terepthlate) (PET), PVC, PE, polypropylene (PP), polystyrene (PS), and polyamide (PA), have been preferably used in food packaging industries due to their low cost and good mechanical performances. In recent years, due to their environmental impact and nonbiodegradability, the synthetically based polymers have tended to be replaced by ecofriendly biopolymers, such as aliphatic–aromatic copolymers (PET/biodegradable polyester sold under the trade name Bio-max by DuPont Tennessee), aliphatic polyesters (trade name: Nodax produced by Procter and Gamble Co. P&G, trade name: Eastar bio produced by Eastam Chemical Company UK), polylactide aliphatic copolymer (CPLA), polycaprolactone (PCL), poly(lactic acid) (PLA) (Natureworks™ PLA produced by Natureworks™ LLC Blair, NB), polyhydroxyalkanoates (PHA) and starch-based polymers (trade names: Biopur® from Biotec GmbH, Eco-Foam® from national Starch & Chemical and Envirofill™ from Norel) have been emerging in food packaging industries [17]. During the processing of polymers, the mechanical, thermal, optical, and other properties have been improved by using optimized processing parameters [18]. The innovative processing technology of the polymer composites has been well developed in recent years. Schmidtchen et al. invented a novel semidry extrusion approach to produce a 100% algae-based packaging material [19]. This process tended to be a cost-efficient processing method since it reduced the moisture content by 80% and prevailed over the drawbacks of a solution-casting method. González et al. combined both extrusion and compression techniques to produce thermoplastic starch nanocomposite films with excellent transparency and better mechanical and barrier properties [20]. Electrospinning is a newly emerged and versatile process to produce polymeric nanofibers with a large surface area, high porosity, and high molecular orientation, thus making it suitable for a food packaging application [21].

This paper intends to present a comprehensive review of active agents incorporated in both synthetic and natural substrates used for enhancing the antioxidant and the antimicrobial properties of the polymer matrix as well as the bulk processing technologies involved in the food packaging applications during the last 10 years. A pictorial representation of the linear and circular economy of bioplastics is explained in Figure 1 [22].

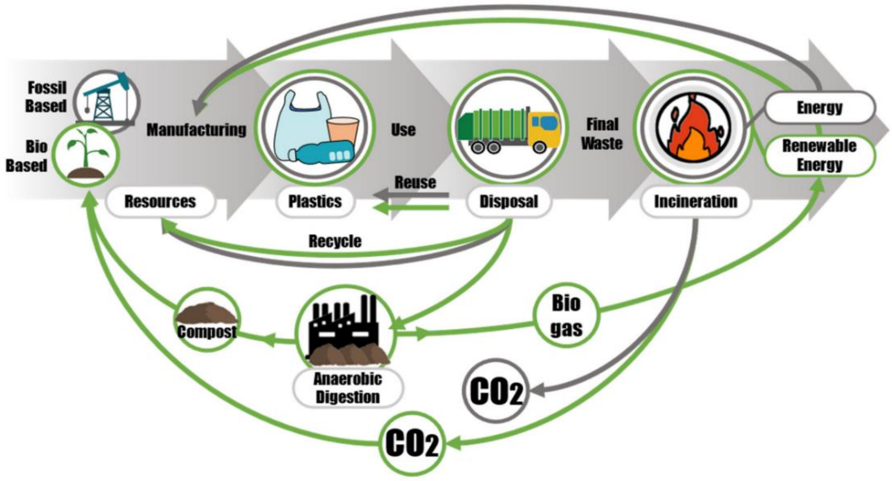

Figure 1. An infographic representation of the linear and circular economy of bioplastics. Reproduced from ref [22].

2. Bulk Preparation Technologies

The different types of polymer processing technologies widely used in packaging industries are compression molding, injection molding, extrusion molding, blow molding, thermoforming, and electrospinning.

2.1. Compression Molding

Compression molding is the oldest material processing technique used in the industrial, commercial, and consumer parts manufacturing process for high production volume for both thermoplastic and thermoset polymers. Thermoplastics such as ABS, nylon, polycarbonate, polyethylene, polypropylene, polystyrene, and various blends are used for compression molders. In addition, thermosets such as epoxy, phenol-formaldehyde, and elastomers are also processed in smaller quantities [23]. This process is mainly used to produce screw caps for bottles, sheets for food containers, and other liquid containers in the food packaging industries. This process delivers products with increased mechanical resistance, insolubility, and thermal stability in the curing or cross-linking process due to the presence of both pressure and heat [24]. Bulk molding compound (BMC) and sheet molding compound (SMC) and produced from thermosetting polymers, while glass mat thermoplastics (GMT) are produced from thermoplastic compounds through compression moldings. Figure 2 illustrates the uniform and nonuniform plates produced by compression molding. Mold A produces uniform plates due to its flat surface in the upper and lower molds, whereas Mold B produces nonuniform plates with a thin section, stepped section, and thick section [25]. In both types of compression molding, a hot treatment may be applied, which requires both pressure and temperature, as well as a cold treatment, which requires only pressure. [26]. Xie et al. produced highly flexible starch-based films with [Emim][OAc] as plasticizer, which inhibited the bacterial attack using a simple melt-compression molding process [27]. The main advantage of a compression molding process is that it can be performed even when the viscosity of the final formulation is not very low [28].

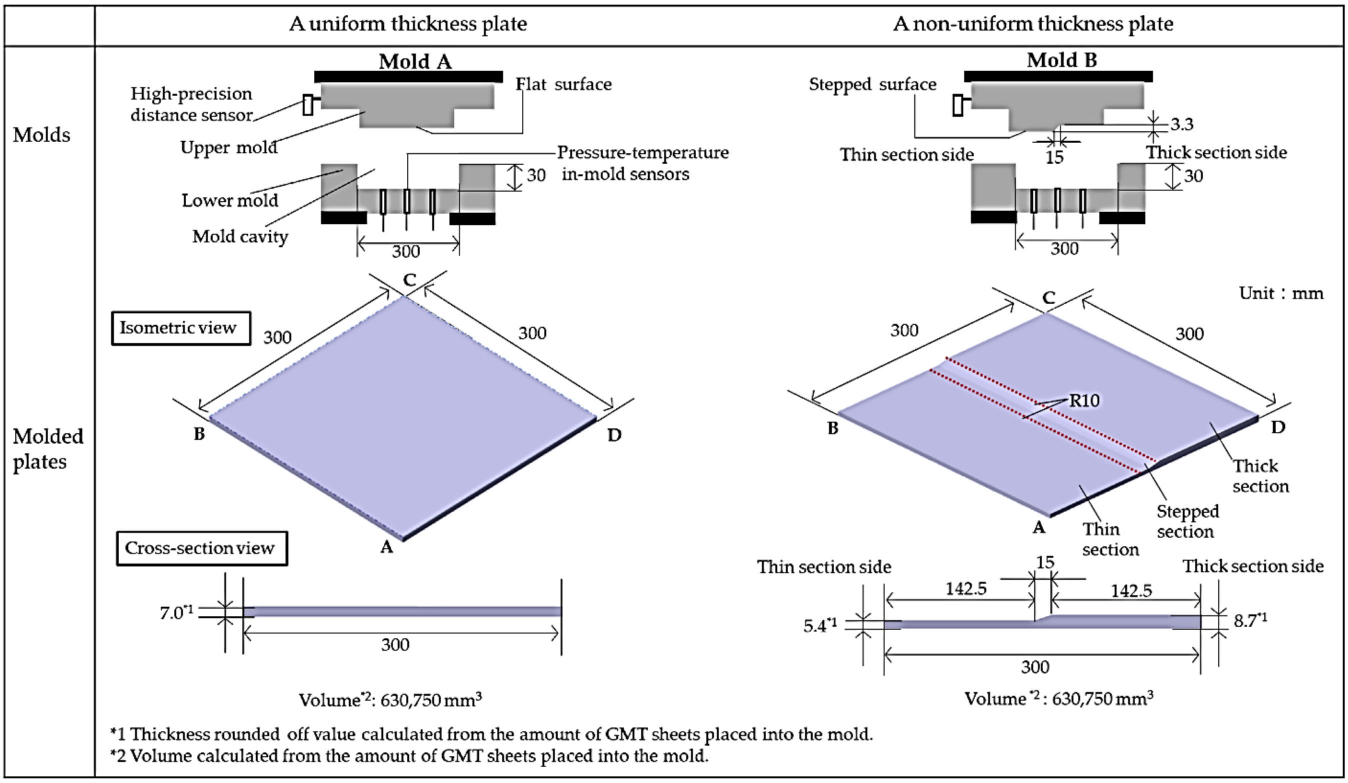

Figure 2. Schematic illustration of compression molds and dimension of molded parts. Reproduced from ref [25].

2.2. Injection Molding

Injection molding is the oldest and most widely used manufacturing technique to fabricate products with complex shapes and surface smoothness. Polymers such as PET, PP, high-density polyethylene (HDPE), and LDPE are widely injection-molded to produce preforms, jars, and containers in packaging industries [24]. Pavon et al. successfully produced rigid food packaging materials with poly(butylene adipate-co-terephthalate) (PBAT) blended with two pine-resin derivatives (gum rosin (GR) and pentaerythritol ester of GR (UT)) by an injection molding process [29]. During this process, the polymers were heated up to an elevated temperature and pushed into a mold cavity with a high pressure to obtain the desired shape. Clamping, injecting, cooling, and ejecting are the important processing steps of injection molding [30]. This method can be used for the incorporation of reinforcement agents or other additives into polymer granules. In composite manufacturing, the additive is incorporated into the polymer matrix through extrusion or internal melt technique and finally processed by injection molding to obtain the desired shape [31].

2.3. Extrusion Molding

Extrusion molding is the most preferable option in the food packaging industry due to its great design flexibility, low production costs, and its postproduction operations, since it does not necessitate any additional curing time [32]. Polymers such as PET, polylactic acid (PLA), PE (low- and high-density), PS, PP, and cellulosic derivatives are commonly used in extrusion molding to manufacture food and beverage containers as well as packaging films [33]. It is the most popular process for continuous production of fixed cross-sectional shaped objects in the plastic industry as shown in Figure 3 [34]. The polymer, in the form of pellets or flakes is heated and forced into a long tubelike shape-molding machine using a screw extruder. The screw is a determinant factor of the extruder's performance. The length and diameter (L/D) ratio of the screw is sectioned into feeding, compression, and metering zones. It also determines the mixing and uniformity of the process. The screw rounds per minute (RPM), screw configuration, temperature, and melt viscosity play an important role in the output rate of the extruder. Finally, the extruded object is cooled and ejected to produce shaped products such as films (blown or cast films), sheets, wires, tubes, drinking straws, synthetic and optical fibers, etc. Considering that extrusion molding is the most frequently used industrial technology for food packaging applications, this review focuses on a state-of-the art analysis of extrusion in active packaging. Section 5 provides a detailed discussion of the manufacturing of food packaging film using the extrusion method with active agents incorporated.

2.4. Blow Molding

Blow molding is a process of forming a hollow object by inflating it with air using an extruder or thermoplastic molten tube called a parison. The air-blown tube acquires the shape of the mold, and the formed parts are cooled in the blow mold taking the desired shape without wrapping. The blow molding consists of three types, namely, extrusion blow molding, stretch blow molding, and injection blow molding. Stretch blow molding has numerous advantages such as a low cost, a low gram weight, the optimization of the preform design, durability, and a high-volume production [35]. The extrusion blow molding is a workhorse process of polyolefins such as HDPE and PP, to produce plastic containers such as bottles, jars, and containers, as shown in Figure 4 [36]. PET resins are not suitable for this method. It is classified into two major categories namely continuous extrusion and intermittent extrusion. Injection blow molding is a process where the resin is injected into a preform cavity through a horizontal screw and the parison is blown into the final shape and cooled. Resins such as HDPE, PS, PET, and PVC are used for producing bottles via injection blow molding [24]. The core rod carrying the product is heated to 120 °C and the strip bar removes the final product. Stretch blow molding is used to manufacture poly(ethylene terephthalate) (PET) bottles for the soft-drink beverage industry. In this process, the parison or preform is stretched in both axial and hoop directions.

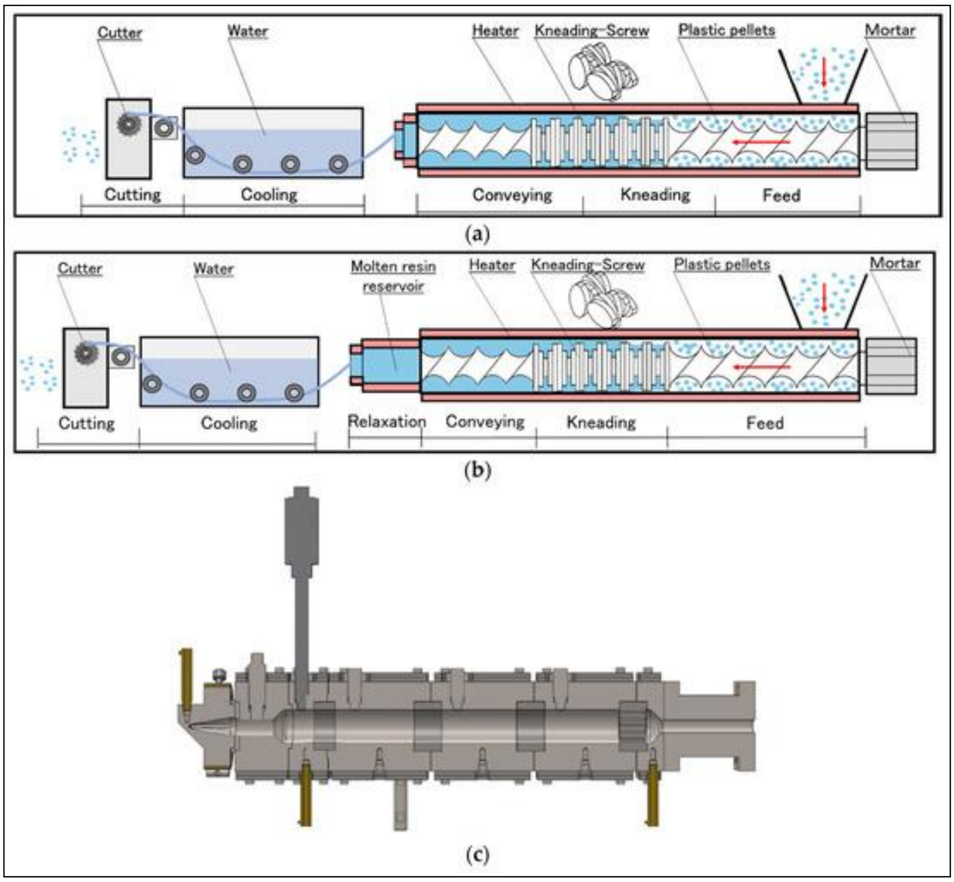

Figure 3. Schematic of the screw extruder (**a**) without and (**b**) with the molten resin reservoir, and (**c**) cross-sectional schematic of the molten resin reservoir. Reproduced from ref [34].

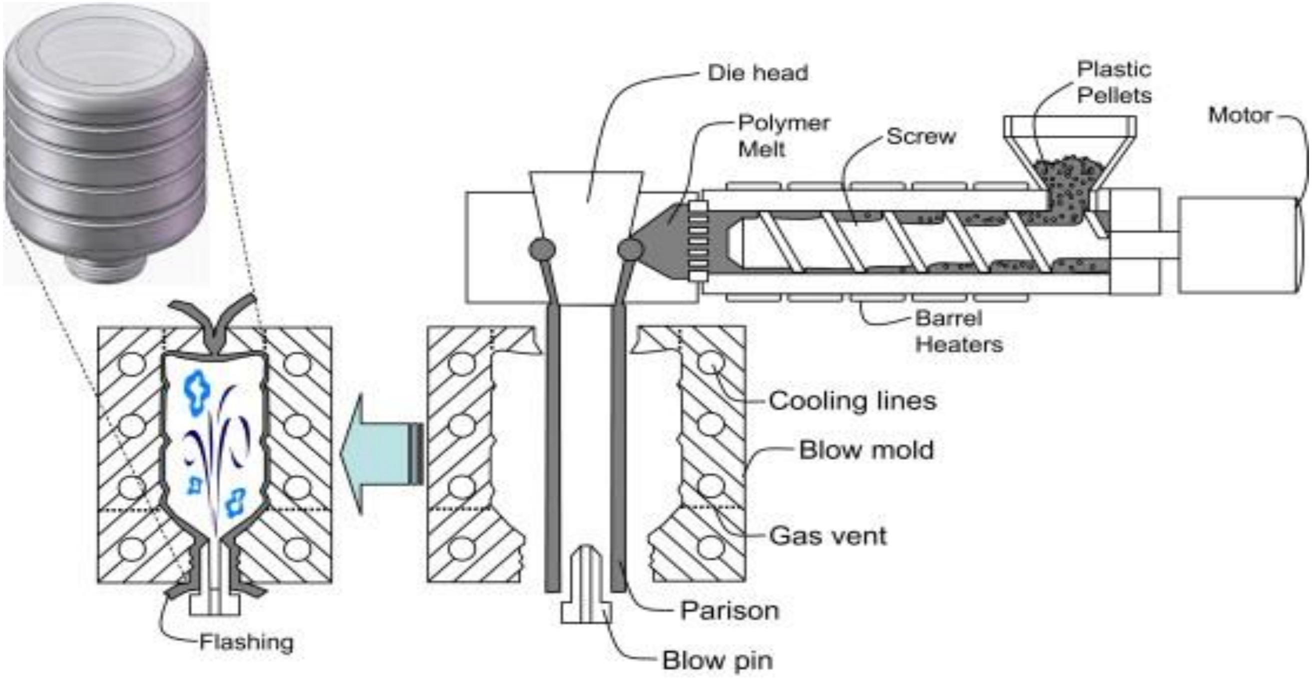

Figure 4. Plastic blow molding process. Reproduced from ref. [36] with permissions from Elsevier. 2017.

2.5. Thermoforming

Thermoforming is a rapidly emerging technique to produce plastic packaging due to its low tooling and operational cost. High-impact polystyrene (HIPS), ABS, PVC, PP, HDPE, and polycarbonate are used for manufacturing thermoformed cups and bowls. Polystyrene is thermoformed to produce salad bar containers, cups, cutlery, yogurt, cottage, and cheese containers. Crystallized polyethylene terephthalate (CPET) is used to produce containers for baked products such as muffins and cakes. PS blended with poly (phenylene oxide) (PPO) is used in the manufacturing of thermoformed trays and containers [37]. During this process, the plastic sheets are heated slightly above their glass transition temperature or melt temperature against a rigid single surface mold followed by cooling and trimming processes to form a three-dimensional product with a high surface area. Forming time and temperature play a vital role in the surface quality and shrinkage. The thermoforming process is classified into three different methods: mechanical thermoforming, vacuum thermoforming, and pressure or external pneumatic air thermoforming. It is widely used in various industries such as food packaging, automotive industrial building, etc. The development in the processing technologies enables thermoforming to compete with injection and blow molding [38]. The system between tray sealer and cutting machinery is illustrated in Figure 5 [39].

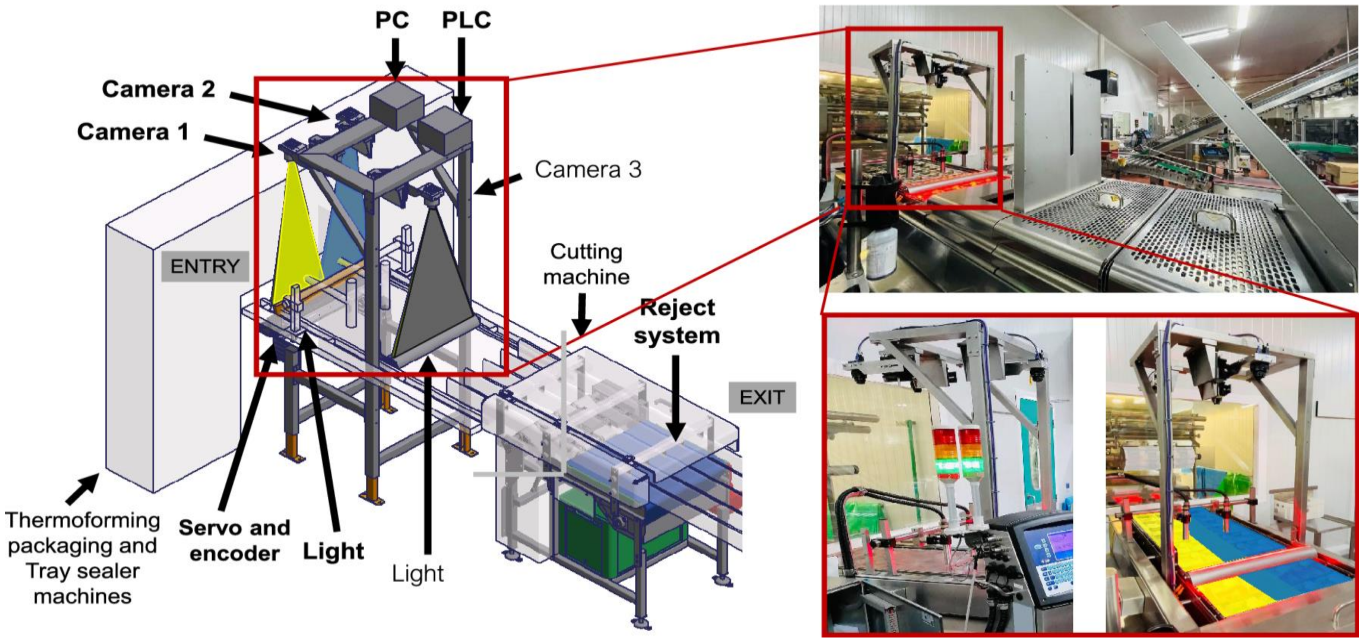

Figure 5. An illustration of the major elements of the suggested computer vision system, with views of the genuine scenario (bold). A servo and an encoder attached to a programmable logic controller (PLC) regulate the speed at which the food packages move, the position of the items, and the timing at which the reject system must be activated. The cameras are positioned between the tray sealer and the cutting equipment. Images for the sealing test are acquired by triggering monochrome line scan cameras 1 and 2 at various exposure periods. Images for the serigraphy and traceability tests are captured using camera 3. Then, after the photographs have been acquired, the reject system is processed to determine how to move forward. Reproduced from ref. [39] with permission from Springer Nature, 2021.

2.6. Electrospinning

Electrospinning is an eloquent technique used to produce polymeric fibers in several structures and morphologies. The electrospun fibers are optimized and produced with different morphologies such as normal electrospun fibers, spring/helical electrospun fibers, porous electrospun fibers, core-shell electrospun fibers, hollow electrospun fibers, Janus electrospun fibers, triaxial electrospun fibers, and others [40]. The antimicrobial agents are incorporated into the fibers to impart the antimicrobial activity of the fibrous mat.

When antimicrobial agents such as silver or copper agents are loaded into fibrous mats, it creates thousands of loading spots due to their large surface area and high porosity. The resultant fibrous mats will exhibit antimicrobial activity [41,42]. The electrospun materials commonly used in food packaging industries are chitosan (antibacterial), corn protein (edible), polyvinyl alcohol (transparent), etc. Biopolymers such as PCL, PLA, natural cellulose, starch, and poly(propylene carbonate) (PPC) have also been electrospun and used in the food packaging field [21]. Briefly, Amna et al. produced an antimicrobial hybrid packaging mat using biodegradable polyurethane mixed with virgin olive oil and zinc oxide via an electrospinning process [43]. Vega-Lugo et al. fabricated antimicrobial electrospun fibers from a soy protein isolate (SPI)/poly(ethylene oxide) (PEO) blend and PLA with the addition of allyl isothiocyanate (AITC) into fiber-forming solutions for active food packaging applications [44]. The steps involved in the electrospinning process are: (1) the formation of a Taylor cone or cone-shaped jet by charging the liquid droplets; (2) the extension of the charged jet; (3) the thinning of the jet in the presence of an electric field and whipping instability; and (4) the solidification of the jet into nanofibers [45]. It is a thermodynamic process during which the liquid droplets are electrified to produce a jet, followed by stretching and elongation that result in the formation of fibers, as shown in Figure 6 [46]. The electrospun fibers exhibit a very high surface activity which is required for active packaging applications. The possibility to vary the structure and the morphologies of the electrospun fibers results in improved mechanical and barrier properties. It also protects the active agents loaded in the electrospun fibers [47].

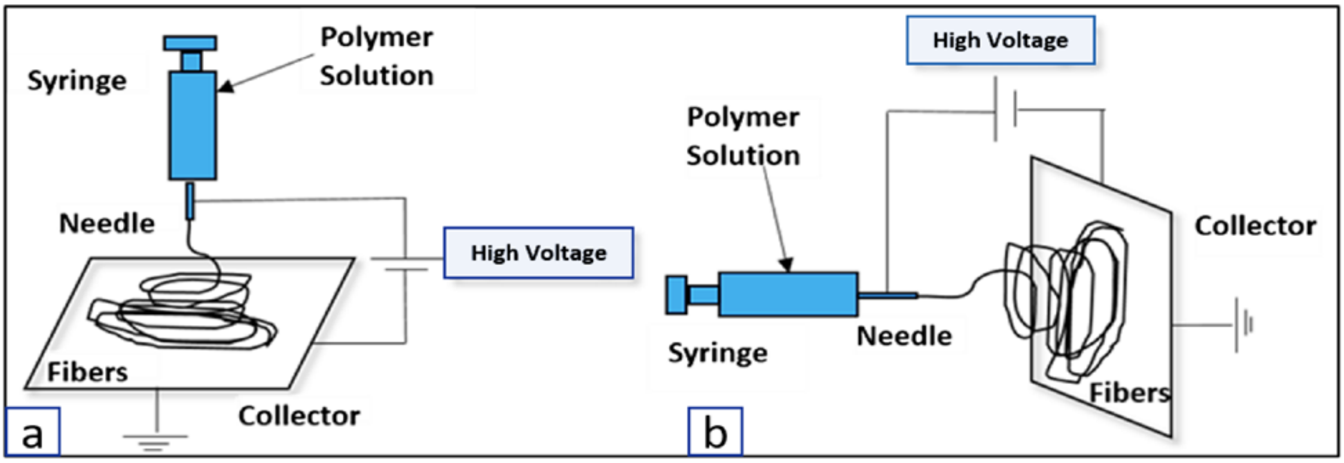

Figure 6. (**a**) Schematics of electrospinning apparatus of vertical setup and (**b**) horizontal setup Reproduced from ref. [46].

3. Active Agents incorporated in Bulk Preparation Technologies

Active packaging can be achieved by the addition of active agents into the polymer using several methods, such as the addition of sachets, a coating of the polymer, surface immobilization through covalent/ionic linkages, or direct incorporation. However, the most used method is the direct incorporation of active compounds into the bulk of the polymer through extrusion. It ensures the uniform distribution of the active compounds throughout the matrix of the polymer and avoids any direct contact of the compounds with the food [48]. However, the additives used in packaging must be wisely chosen so that they comply with the requirements of regulatory agencies, such as the Food and Drug Administration (FDA) and the European Food Safety Authority (EFSA). Therefore, active ingredients are included into food packaging if they support one or more of the following attributes, such as mechanical or barrier capabilities that increase shelf life or antibacterial, antioxidant, or antiviral properties. Additionally, the enhancement of qualities such as transparency would be advantageous because it would make food more accessible and appealing to customers.

Understanding the mechanism of action of antibacterial agents and antioxidants are of great importance while their addition in bulk preparation technology is considered. The release of ions, reactive oxygen species (ROS), and electrostatic interactions with the cell walls of bacteria are the prospective explanation for the active mechanism of antibacterial agents. Antioxidants can delay spoilage by slowing both lipid oxidation and protein denaturation by reducing the amount of oxygen in food systems. Additionally, they stop the oxidation chain reaction, hinder the further development of the oxidation reaction, and inhibit or deactivate the activity of the enzymes that promote the oxidation reaction. The best antioxidants for use in active packaging should be affordable, nontoxic, highly active at low concentrations, and highly permeable and should have a good stability. Additionally, they should not have a negative impact on the food's quality, such as taste or odor. The active substances should have a low molecular weight because they are intended to diffuse through polymer macromolecules. As a result, the release rate is influenced by their physical size, with larger active compounds releasing at a slower rate than smaller ones [49].

Various active agents have been studied in the past few decades, ranging from metal ions and metal oxides, such as silver, copper, TiO_2, and ZnO, to essential oils, bioactive components, such as thymol and carvacrol, and enzymes, such as nisin and lysozyme. Nevertheless, all the bulk preparation techniques involve high-temperature processing, which is why the fillers are also required to be thermally stable. Based on their origin, fillers could be broadly classified into natural and synthetic active agents [50]. A list of some of the active agents extensively used during the past decades in bulk preparation methods is listed in Table 1.

Table 1. Active Agents Widely Used for Bulk Preparation Methods.

Active Agents	Advantages	References
ZnO	Low-cost, high ultraviolet absorption capability, and strong antibacterial activity on a wide range of bacteria	[51–53]
TiO_2	Enhances ethylene-scavenging activity	[54–56]
Nanoclays	Improved mechanical, gas barrier, optical properties at low filler content	[57–59]
Nanosilver	Antimicrobial activity	[60,61]
Catechin	Antioxidant and antimicrobial activities	[62,63]
Curcumin	Excellent antiviral, anticancer, antimicrobial, anti-inflammatory, and antioxidant activities.	[64,65]
Essential oils	Antioxidant, anticancer, and antimicrobial, cost-efficient	[66–69]
Lignin	Excellent antioxidant and antimicrobial activity attributed to the large number of phenolic groups; mechanical properties and fire-resistance	[70–72]
Tannin	Antioxidant and antimicrobial activities	[71,72]
Gallic acid	Oxygen-scavenging ability	[73,74]

3.1. Inorganic Active Agents

3.1.1. Metals and Metal Oxides

Inorganic particles are thermally stable and thus can be easily incorporated into polymers using bulk synthesis methods such as extrusion, blow molding, etc., for active packaging applications. Metals and their ions have been known for their "antimicrobial" action for decades and are still employed as active agents, especially in their nanoforms. Silver (Ag), copper (Cu), zinc (Zn), gold (Au), and titanium (Ti) are the major metals emerging as active agents owing to their low toxicological effects [75]. One of the generally accepted mechanisms of antimicrobial activity of metal oxides is that the microorganisms are thought to have a negative charge, whereas metal oxides have a positive charge. As a result, the microbe and the packaging form an "electromagnetic" attraction. When bacteria come into contact with the package surface, they are rapidly oxidized and killed [76].

Carbone et al. studied the "antimicrobial", antifungal, and antiviral activities of silver nanoparticles (NPs) [77]. Furthermore, it was reported by Ahari et al. that the film permeability, the product quality, and the mechanical properties of the films were improved by the incorporation of silver NPs [78]. Conversely, copper NPs are preferred over silver nanoparticles as they are easy to synthesize and inexpensive. Copper NPs have been successfully incorporated into various matrixes such as HDPE, low-density polyethylene (LDPE), cellulose, etc., using bulk synthesis methods such as extrusion and blown molding by various researchers [79]. Bikiaris et al. developed HDPE/Cu-nanofiber nanocomposites and observed their effect on mechanical, oxygen barrier, and antibacterial properties by varying the percentage of Cu nanofiber. The mixture of three kinds of bacterial strains, that is, *Escherichia coli DHSa*, *Pseudomonas fluorescens BS3*, and *Staphylococcus aureus* strains, was used for the antibacterial studies. It was observed that the sample containing 2.5 and 5% of Cu nanofiber showed better properties. The resultant material was suitable for food packaging applications. Figure 7 depicts the distribution of Cu nanofibers in the HDPE matrix and the growth of bacterial colony forming units (CFU) on various concentrations of Cu nanofibers [80].

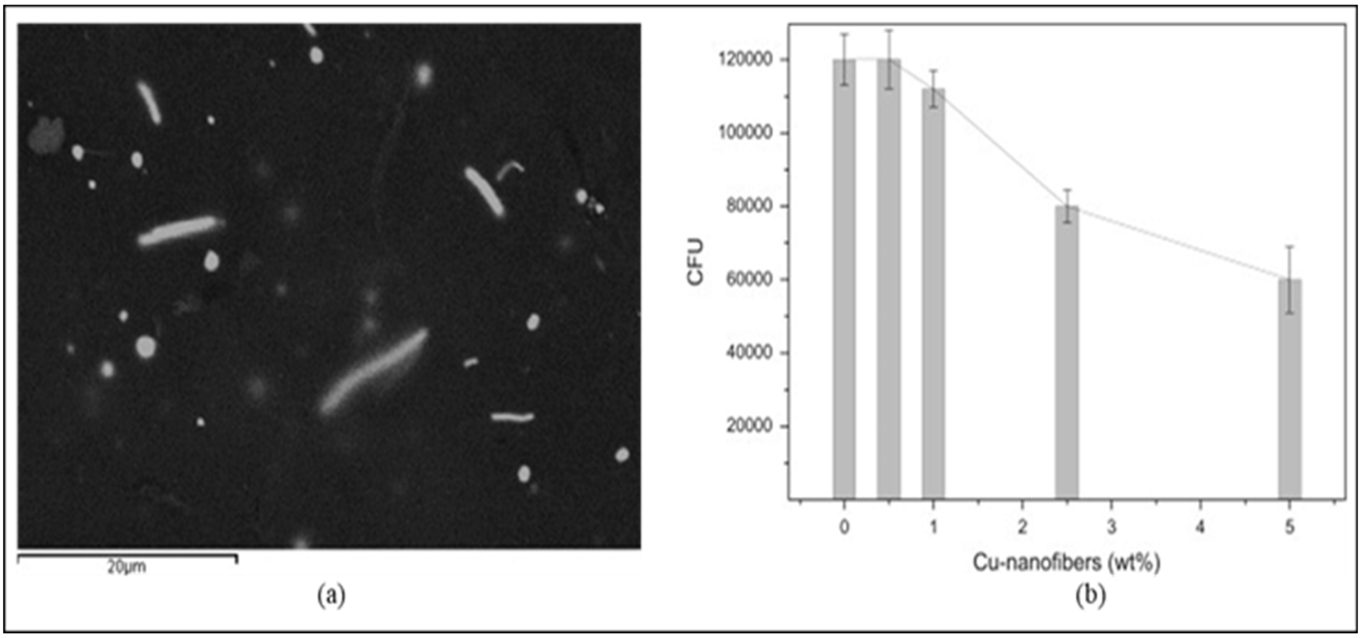

Figure 7. (**a**) SEM images of HDPE/Cu-nanofiber nanocomposites containing 2.5 wt % Cu nanofibers. (**b**) Growth of bacterial colony forming units (CFU) in nanocomposites containing different amounts of Cu nanofibers during an incubation time of 24 h. Reproduced from ref. [80] with permission from Elsevier. 2013.

Metal oxides, such as titanium dioxide (TiO_2), zinc oxide (ZnO), and magnesium oxide (MgO), are widely used in active packaging materials for their bactericidal properties [81]. They belong to a category of materials that are generally recognized as safe (GRAS) by the FDA. Mallakpour et al. reported that ZnO NPs were proven to enhance the thermal stability as well as the mechanical and barrier properties of a wide variety of polymers, such as polyamides, polyimides, polyurethanes, polyethylene, etc. [82]. These properties made the polymers appropriate for food packaging. Thermal and mechanical stability is important for active agents as the packaging film processing techniques involve high-temperature and high-shear processing conditions. Barrier properties are exceptionally important because the permeation of gases such as O_2 and CO_2 might cause food spoilage. Esmailzadeh et al. evaluated the antibacterial effect of LDPE containing ZnO nanoparticles [83]. The composite film was prepared by feeding both ZnO NPs and LDPE pellets to a twin-screw extruder at varying ratios. Composite film containing 4 wt. % of ZnO was observed to have stronger inhibitory effect against *B. subtilis* (Gram-positive) bacteria. The migration of Zn^{2+} ions was also studied and found to be negligible, hence not hazardous for food consumption, thus making it conceivable for safer food packaging.

Emamifar et al. studied the synergistic effect of silver and ZnO nanoparticles on the inactivation of *Lactobacillus plantarum*. LDPE nanocomposite films were prepared using single screw blown film extrusion by adding both Ag and ZnO NPs at a mass fraction of 10% to the LDPE pellets. The obtained films were used to pack orange juice inoculated with *Lactobacillus plantarum*. Nanosilver paired with ZnO nanoparticles exhibited a better inhibition of *Lactobacillus plantarum* and was thus proved suitable for prolonged storage. It was observed that as the nano-ZnO concentration increased to 1%, the antimicrobial activity decreased, while an increased concentration of Ag NPs increased the antimicrobial activity. LDPE with 5% P105 (TiO_2 95% + metal nanosilver 5% with particle diameters of about 10 nm) packages demonstrated a superior antimicrobial activity compared with others, as shown in Figure 8 [84].

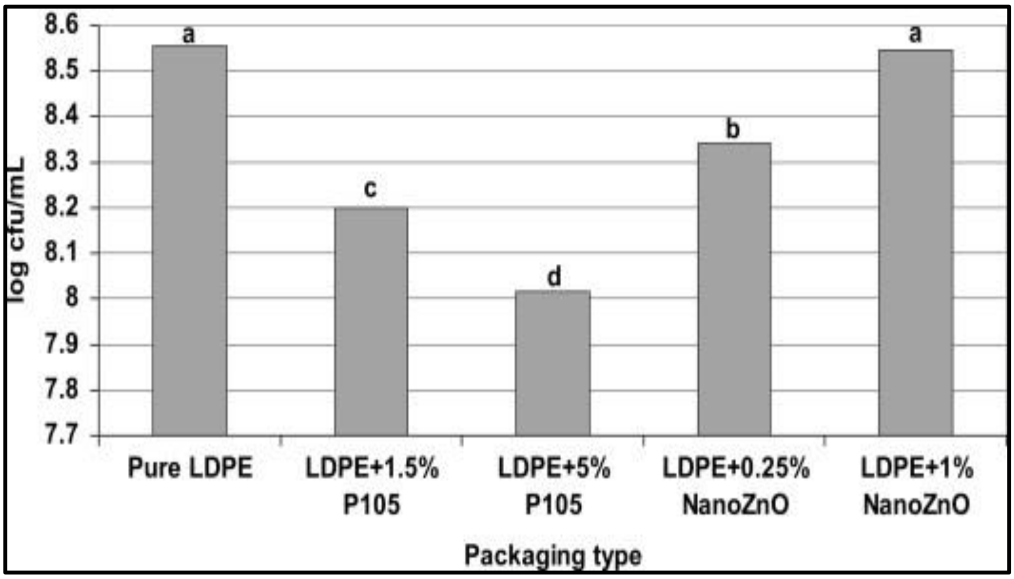

Figure 8. Effect of packaging type on inactivation of *Lactobacillus plantarum*. Reproduced from ref. [84] with permission from Elsevier. 2011.

In a recent work by Esmailzadeh et al. a comparative study of antibacterial activities of CuO/LDPE and ZnO/LDPE nanocomposites was carried out [85]. It was observed that the film with CuO particles showed stronger antibacterial effects on both *Bacillus subtilis* and *Enterobacter* aerogenes, which are the common causative microorganisms for the spoilage of bread, vegetables, and meat, in comparison with the ZnO-containing film. However, the work confirmed that both compounds were appropriate for active packaging, due to the stability during the extrusion and their antibacterial activity.

A PE/TiO_2 nanocomposite film prepared by Xing et al. was found to be effective against *Staphylococcus aureus* bacteria [86]. The tensile strength and elongation at break of the PE film was also improved by the addition of TiO_2 nanoparticles. Additionally, the composite film exhibited a higher exchange of water molecules compared to neat PE and thereby reduced the high relative humidity inside the packaging. This improved the shelf life of some fruits with high respiratory rates.

Silver nanoparticles (AgNPs), zinc oxide, and TiO_2 were used as fillers in PLA composites by Tarani's group, who investigated the cold crystallization kinetics and heat degradation of these materials [87]. A thorough analysis of processes such as crystallization, nucleation, degradation, and their kinetics was conducted upon the nanocomposites with 1 wt. % of each filler. The results showed that metal oxide nanofillers catalytically altered the thermal degradation and the crystallization of PLA samples.

In a different work by Črešnar et al. the effect of Ag, ZnO, and TiO_2 nanoparticles at different loadings (0.5, 1.0, and 2.5 wt. %) into PLA samples by a melt-mix extrusion method followed by film formation was illustrated [51]. It was observed that the chemistry, morphology, and wettability of the surface were all impacted by the addition of NPs during the melt extrusion process, which also had an impact on the antibacterial effectiveness and mechanical properties of the PLA nanocomposites. The NPs were distributed near the surface region as well as in the depth of the bulk itself and improved the surface roughness. Moreover, it was also observed that all PLA–NPs film exhibited improved mechanical properties.

There have been numerous studies conducted by the scientific community investigating metals, metal oxides, and their combinations as active agents. There is a wide variety of branded and unbranded goods from various countries available in metal and metal oxide forms incorporated into active packaging nowadays. For instance, FresherLonger™ is a U.S.-based company which develops a nanosilver-reinforced PP packaging material which extend the food shelf life [88]. Ageless® from Mitsubishi Gas Chemical Co. Ltd. is a Japan-based active packaging film containing iron as an oxygen scavenger [89]. Furthermore, it is a common belief that the packaging materials significantly contribute to the cross-contamination and the indirect transmission of viral infection. Moreover, seafood, vegetables, and fruit items may be contaminated by viral pathogens, which is a major factor in the spread of viral infections [90]. Finding appropriate, alternative, safe, and biocompatible antiviral agents is of critical importance for stopping the spread of infections and minimizing financial losses, since viral diseases pose a serious threat to both the human health and the economy. In general, nanoparticles with notable antibacterial and antiviral properties include silver nanoparticles, gold nanoparticles (AuNPs), quantum dots (QDs), carbon dots (C Dots), graphene oxide (GO), silicon materials, polymeric NPs, etc. The development of antiviral materials, including active coatings, films, and multilayer packaging systems, has been the focus of researchers in the past decade, especially after the outbreak of SARS-CoV-2 [91].

Numerous nanoparticles have been found to exhibit a remarkable antiviral action. Even though the literature is scarce, there are reports that silver nanoparticles bind to the glycoprotein surfaces of viruses, preventing them from adhering to and interacting with the intended host cell. Silver nanoparticles are known to produce reactive oxygen species (ROS), which have an antiviral effect [92]. Zinc oxide nanoparticles have proven to possess antiviral properties by many studies. HSV1, HSV2, and H1N1 viruses when exposed to surface-modified zinc oxide nanoparticles cannot be replicated. Zinc oxide nanoparticles are known to have antiviral effects by releasing Zn^{2+} ions in host cells and increasing their intracellular concentration, which hinders the reproduction of several RNA viruses. This is in addition to preventing the contact between virions and host cells [92]. Additionally, copper oxide has been used to prevent viral infections [93].

3.1.2. Nanoclays

Hydrous aluminosilicates with nanoparticle sizes constitute the majority of clay minerals. They have desirable qualities such a tendency for dispersion, a large surface area, hydrophilicity, biodegradability, and a regulated polymer interaction with the matrix, all of which are crucial for applications in food packaging. The use of nanoclay could enhance the physical, chemical, mechanical, thermal, and barrier properties of the polymer matrix. Food packaging made of clay has improved gaseous, moisture, and odor barrier properties, as well as improved transparency and durability [94]. Montmorillonite (MMT) and halloysite (HNT) are the most used nanoclays in food packaging applications, having platelet and tubular structures, respectively. Montmorillonites are natural aluminum magnesium silicate clay and halloysites are natural aluminum silicate nanoparticles. They are either utilized as fillers in films or as carriers for volatile active agents [95]. Other nanoclay materials that have been used for active food packaging include bentonite, kaolinite, hectorite, sepiolite, saponite, vermiculite, and rectorite. Bentonite clay is made up of a silicate layer that contains calcium and sodium ions in a 2:1 ratio. Kaolinite is a phyllosilicate composed of an octahedral aluminum hydroxide and a tetrahedral silicon oxide sheet in a 1:1 ratio. Sepiolite is also a phyllosilicate and is also known as hydrated magnesium silicate. Rectorite clay has the structure of both MMT and mica, with a dioctahedral micalike layer (nonexpandable) and a dioctahedral montmorillonite-like layer (expandable) in a 1:1 ratio [96]. Vermiculites are 2:1 layered silicate, with layers built up of one octahedral sheet sandwiched between two tetrahedral sheets [97].

Tas et al. reported the effect of HNTs and PE pellets extruded to obtain a PE/HNT nanocomposite film. The resultant films were observed to exhibit ethylene-scavenging capacity and excellent barrier properties. The films were also proven successful for slowing down the ripening of bananas and tomatoes due to their ethylene-scavenging properties. Additionally, films were experimented on strawberries and chicken fillets on which they slowed down the weight loss and bacterial growth, respectively, owing to their water vapor and oxygen barrier properties [98].

Tornuk et al. grafted nanoclays with essential oils and incorporated them into linear low-density polyethylene (LLDPE) pellets to make novel active films [99]. Both HNTs and MMTs were loaded with thymol (THY), eugenol (EUG), and carvacrol (CRV), using Tween 80 as the surfactant. These active agent-loaded nanoclays were then added to the LLDPE pellets (5 wt. %) from the same feeding port of the extruder, and nanocomposite films were obtained. Grafting prevented the essential oil compounds from thermal degradation and evaporation during the extrusion process. The films were proved effective against microbes and exhibited remarkable antioxidant properties. Active nanoclay incorporation slowed down the weight loss and raised the melting point of LLDPE, as determined by DSC and TGA tests while lowering the degree of crystallinity. The oxygen permeability of the films was reduced by active nanoclay inclusion, and particularly HNT-incorporated films presented lower permeability values than MMT-containing samples.

Similarly, Busolo et al. developed nanocomposite films with preincorporated resveratrol into MMT and LLDPE via extrusion. The resultant composite films exhibited a strong antioxidant ability coupled with an antibacterial activity. They were proven successful in extending the shelf life of meat as shown in Figure 9 [95].

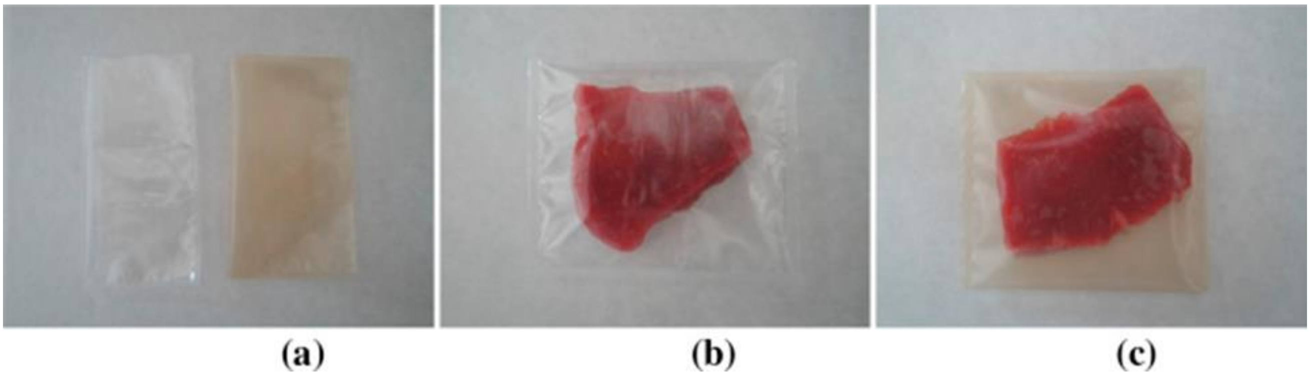

Figure 9. Comparative images of tested films (**a**); sample of meat packaged with blank film (**b**) and, with active film (**c**). Reproduced from ref. [95] with permission from Elsevier. 2015.

Hadj-Hamou et al. synthesized antimicrobial poly(e-caprolactone) (PCL)/bentonite nanocomposite films with enhanced mechanical and water vapor barrier properties for food packaging. The melt blending of PCL with 3 wt % of bentonite and organically modified bentonite was carried out using a twin-screw microextruder. The results showed a reduction in the thermal stability of organically modified bentonite/PCL composites while there was a significant increase in the degradation rate as compared to pure PCL. The decomposition's kinetic study showed that the apparent activation energies of the PCL nanocomposites were lower compared to those of pure PCL [100].

NanoBioMatters Industries S.L, Spain, has utilized kaolinite to develop active agents which exhibited O_2-scavenging properties and is commercially available under the name O2Block®. It is a surface-modified kaolinite that is functionalized with active iron which is claimed to be available to get dispersed in any packaging polymer system [101]. BactiBlock®, an antibacterial additive for raw materials based on polymers, is also produced by the same company. The patented and patent-pending BactiBlock® technology uses silver-functionalized kaolite to create a highly potent antimicrobial solution that is organically derived. BactiBlock® is a powerful tool against odors and stains for food packaging due to its capacity to be dispersed in virtually any polymer matrix and its capacity to inhibit the growth of bacteria, mold, fungus, and other microorganisms [102].

Hundáková et al. utilized modified vermiculites as fillers to develop PE composite films. The resultant films exhibited appreciable activity against E. faecalis. Moreover, there was an improved tensile strength in comparison with pure PE films and thereby, it could serve a better food packaging material [97].

García-Quiles et al. prepared a biocomposite based on commercial polyhydroxyalkanoates (PHAs) and nanoclays, namely, sepiolite and montmorillonite, by extrusion-compounding with a 26 mm twin-screw extruder, and there was an impressive improvement in mechanical properties, making PHA a potential futuristic material for food packaging [103].

Zeolites are yet another clay compound used for active packaging. Barreda et al. synthesized biodegradable active packaging using blow extrusion where zeolite was used as the ethylene scavenger [104]. Poly (butylene adipate-co-terephthalate) (PBAT), glycerol, zeolite, citric acid, and cassava starch were fed to the extruder at optimum conditions, and the control film was prepared without the addition of the zeolite. The effect of the resultant packaging was studied on broccoli, and it was concluded that zeolite slowed down the metabolism rate of broccoli stored at 12 °C, which retained its color and vitamin C content for 7 days. In addition, zeolite also increased the elongation at break and decreased Young's modulus of the film in comparison with the control sample. The synergistic effects of Zeolites when combined with other established active agents, such as nisin, chitosan, potassium sorbate (PS), etc., are also under investigation [105,106].

3.1.3. Other Inorganic Compounds

Silica in the form of gel or nanoparticles (SiO_2), potassium chloride (KCl), calcium chloride ($CaCl_2$), sodium chloride (NaCl), calcium sulfate ($CaSO_4$), etc., are some of the commonly used inorganic fillers in bulk processing of polymers. Sometimes, the compounds themselves function as active agent while sometimes they serve as a medium for the active agents to act [107].

To begin with, NaCl particles absorb water vapor to form a NaCl solution when the relative humidity (RH) is above 75% and desorb vapor when the RH decrease. Hence, they are capable of regulating humidity in their surroundings. This property of NaCl particles was applied to PP by Sängerlaub et al. using established processes such as extrusion, foaming, and stretching. PP films impregnated with NaCl at various concentrations were extruded. In the second step, they were foamed and then stretched to improve the porosity, and the resultant effects on moisture absorption and mechanical properties were investigated by comparing foamed and nonfoamed PP. The results suggested that foamed stretched films with 6 wt. % NaCl absorbed a high amount of moisture from the vicinity; moreover, stretching improved the mechanical properties (Figure 10) [108].

Additionally, potassium carbonate (K_2CO_3) was employed as a carbon dioxide scavenger by Ahn et al. while also serving as a catalyst for the action of gallic acid (GA) as an oxygen scavenger. The film containing 1, 3, 5, 10, and 20% of the nonmetallic-based oxygen-scavenging system (OSS), i.e., K_2CO_3 and GA, were fabricated using a laboratory extrusion cast film line. The film containing 20% OSS showed an effective oxygen-scavenging capacity of 0.709 mL/cm^2 at 23 °C [73]. Similarly, Pant et al. used gallic acid with sodium carbonate (Na_2CO_3) as an oxygen scavenger in monolayer films and multilayer films produced by the coextrusion of bio-PE and PLA. A three-step, pilot-scale procedure combining compounding, cast film extrusion, and lamination was used to create a multilayer packaging film. The film was made up of an outer barrier layer (PLA) that lessened O_2 invasion from the environment, a food contact layer (BioPE), an active layer containing the scavenger (BioPE + 15% (*w*/*w*) GA–sodium carbonate mixture), a biobased adhesive, and a scavenger layer (active Layer + BioPE). Reduced O_2 absorption resulted from the addition of GA to a polymer matrix, particularly in the early stages of the process. When compared to commercially available O_2 scavengers, GA exhibited an astonishingly high absorption [109].

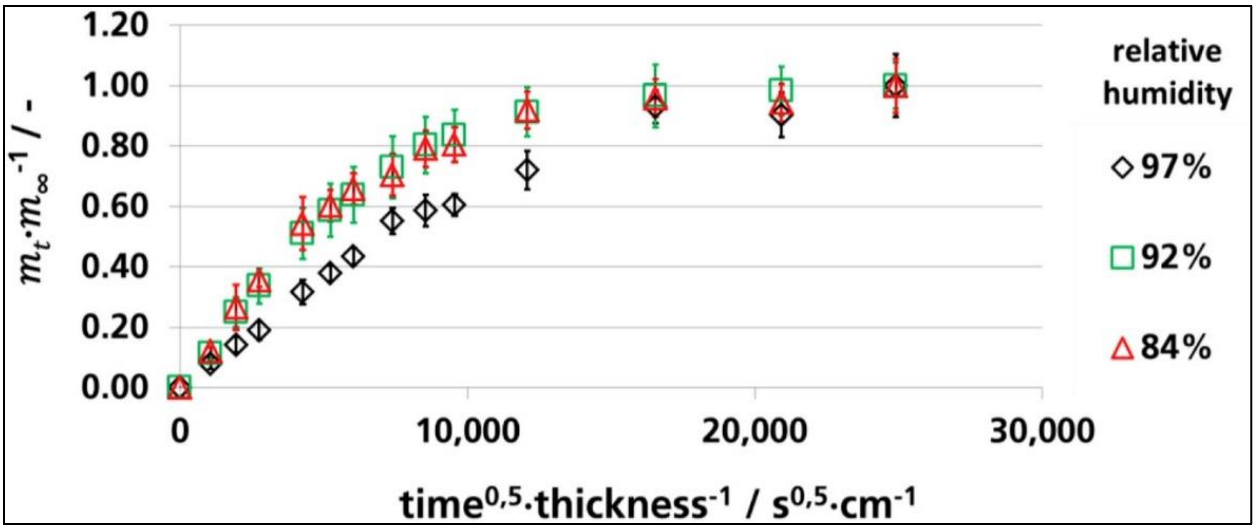

Figure 10. Water vapor absorption at 23 °C; PP with 6 wt. % NaCl, foamed and stretched with stretching factors of 2.5 × 2.5. Reproduced from ref. [108] with permission from Elsevier. 2018.

3.2. Organic Active Agents

Due to rising concern, especially from the consumer point of view, that synthetic additives may contribute to potential health hazards, there is a growing interest on naturally occurring compounds as active agents. Even though, they are thermally unstable, some plant-derived components such as ascorbic acid, carvacrol, tocopherol, lignin, tannin, etc., and some bacteria-derived components, such as nisin, are currently explored as additives in the bulk synthesis of active packaging [107]. The plant-based polyphenolic compounds are widely used for their antibiotic and antioxidant properties. This is due to their ability to donate their phenolic hydrogens to lipid free radicals. However, their thermal instability makes them a hapless candidate for bulk synthesis methods. Despite this, they are currently employed in many active packaging applications directly or indirectly, by coupling them with some stable counterparts [106,110].

Finding appropriate natural active agents that are stable at elevated temperatures and can withstand the high processing conditions of bulk synthetic methods has always been a challenge for the scientific community. Nevertheless, several natural plant extracts, such as flavanols, quercetin, etc., are presently explored for their active compounds. The mechanism of radical scavenging has already been reported by Al Malaika et al. [111]. The tea extracts were detected with the following polyphenol compounds, gallic acid, caffeine, flavanols (catechin, epigallocatechin, epigallocatechin gallate, epicatechin, epicatechin gallate) and five flavanols (myricetin glycoside, quercetin glucoside, quercetin rutinoside, kaempferol glucoside, kaempferol rutinoside), all of which are excellent antioxidants. Amongst all the tea extracts, green tea extract was chosen as an antioxidant for polypropylene extrusion, due to its high content in flavanols and its excellent antioxidant capacity. The melt flow index and the oxidation induction time of the films were measured after multiple extrusions to test their stability. It was observed that the stability of the natural extracts was equivalent to the stability of the synthetic antioxidants, thus showing a potential use of natural antioxidants in the bulk synthesis of polymers [112]. Dopico-García et al. studied the performance of polypropylene samples stabilized with tea extracts in comparison with PP films containing synthetic antioxidants Irganox 1076 and Irgafos 168 [112,113].

Alpha-tocopherol (vitamin E) has been an effectively utilized natural antioxidant in polymer extrusion since 1990s. Various studies have reported the effectiveness, stability, and sustained release of tocopherol in the past decades [114–116]. To take it further, potential active packaging using ecofriendly materials was synthesized by Lopes and his group. Starch/PBAT films reinforced with α-tocopherol were prepared using blown extrusion. Despite the thermal instability of the natural compounds, the films had adequate processability. The inclusion of α-tocopherol improved the transparency of the film and its water vapor permeability apart from the antioxidant property. However, the mechanical properties of the films were not improved [117]. Barbosa-Pereira et al. studied the effects of tocopherol in LDPE and their effectiveness in the extension of the shelf life of fish [118].

Pušnik et al. explored the antioxidant and antibacterial properties of kraft lignin and tannin and their potential contribution to the improved multifunctionality of polylactic acid (PLA) films [72]. PLA based composites were prepared using hot-melt extrusion with the incorporation of lignin and tannin, resulting in a biodegradable film. The composite films exhibited excellent surface mechanical properties as well as antioxidant and antimicrobial activity, which made them suitable for food packaging applications. Furthermore, pomegranate-peel-derived tannin (PPE) was exploited by Hu et al. [119], who prepared double-layer active films with PPE/polyethylene as the inner layer and two different active films with different outer layers, PPE-PE/poly (ethylene terephthalate) (PET) and PPE-PE/PP, and a comparative study was carried out. All three films exhibited a lower microbial growth on pork samples and significant excellent oxygen barrier properties that extended the shelf life. Changes of total viable counts (TVC) during the refrigerated storage period indicated whether it satisfied acceptable cooking standards, as depicted in Figure 11 [119]. The initial TVC of pork steaks for all treatments was from 3.4 to 3.58 log10 CFU/g, indicating that the pork steak was of good quality.

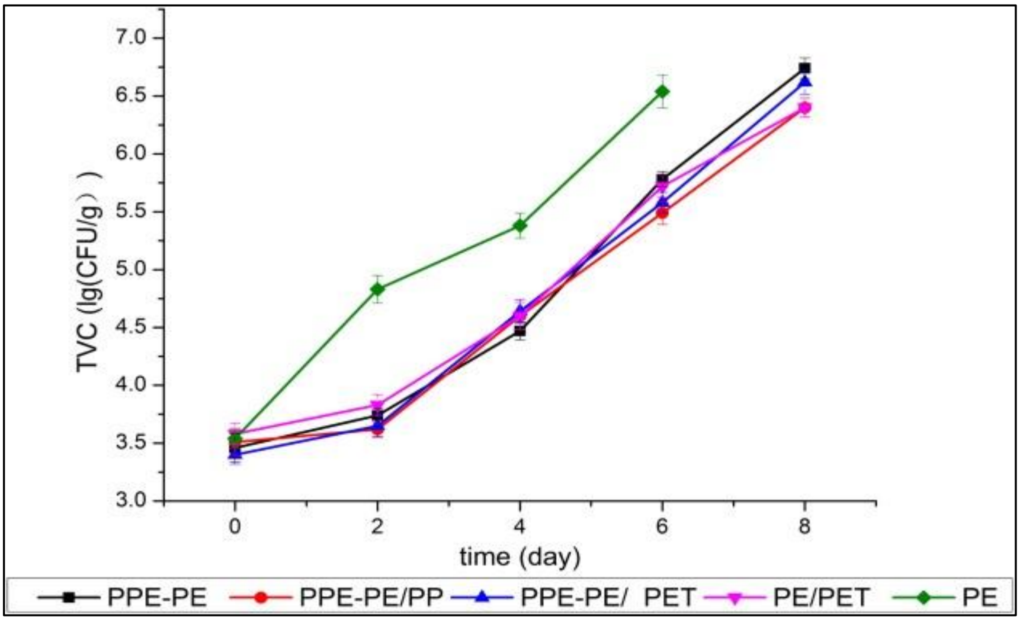

Figure 11. Changes of total viable counts of pork during chilled storage at 4 °C. Reproduced from ref. [119] with permission from John Wiley & Sons—Journals. 2017.

Yang et al. studied the effect of lignin nanoparticles as fillers in PLA based films [120]. They produced films by combining cellulose and lignin nanoparticles with PLA at various amounts, using a twin-screw extruder. The prepared films showed better transparency and mechanical properties (Figure 12). Moreover, they presented a biocidal activity against *Pseudomonas syringae*, a tomato plant bacterium (Figure 13). Thus, it was addressed how the unexplored functionalities of ligno-cellulosic nanoparticles would benefit food packaging. Lignin was used as a filler in bulk techniques other than extrusion [120].

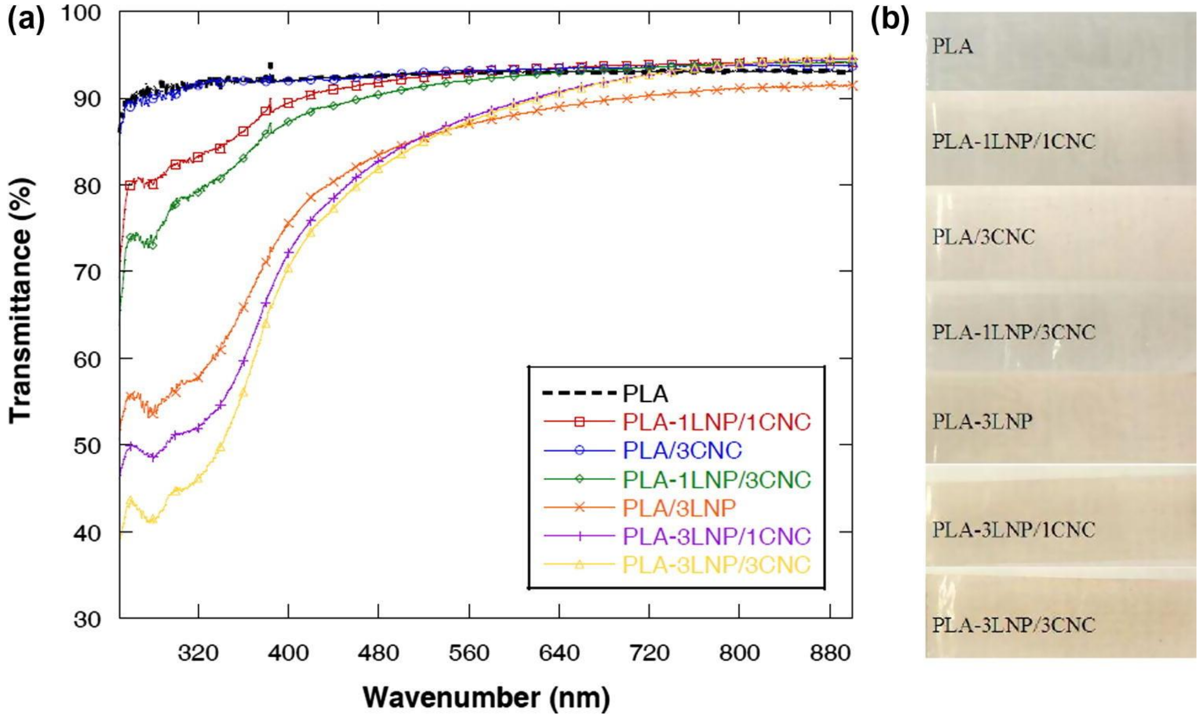

Figure 12. UV–vis spectra of PLA and PLA nanocomposite films containing CNC and LNP nanoparticles in binary and ternary systems (**a**) and visual appearance of the films (**b**). Reproduced from ref. [120] with permission from Elsevier. 2016.

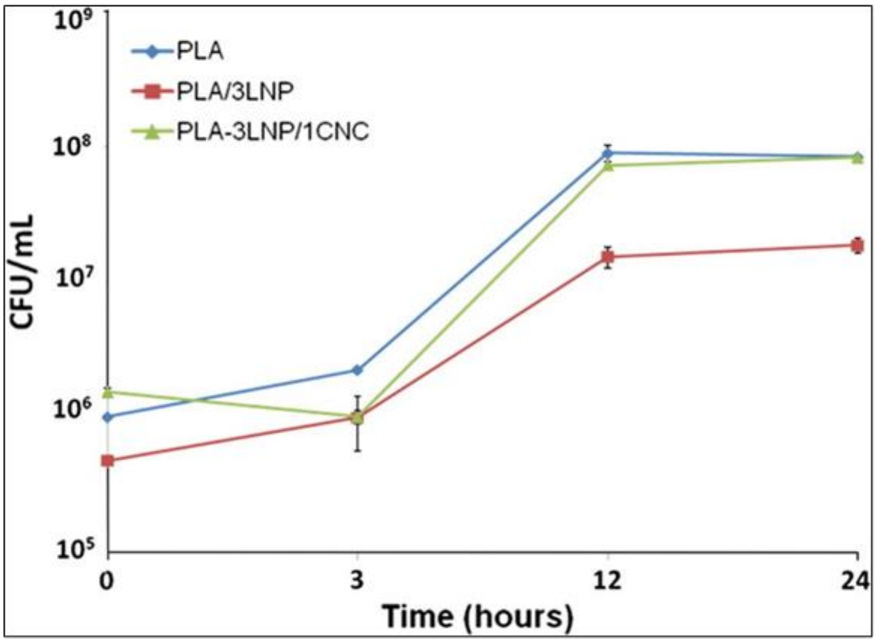

Figure 13. Antibacterial activity of different films based on neat PLA, PLA film with 3 wt.% of lignin nanoparticles (PLA-3LNP), PLA ternary system containing both cellulose nanocrystals (1 wt.%) and lignin nanoparticles (3 wt.%) (PLA-3LNP/1CNC), on the multiplication of tomato plant pathogenic bacteria Pseudomonas syringae pv. tomato (Pst) (CFBP 1323) 1 × 106 CFU/mL. Reproduced from ref. [120] with permission from Elsevier. 2016.

Gallic acid is yet another natural active agent widely employed in bulk processing. There are several reports on gallic acid used as filler in various bulk processing methods, such as the extrusion, lamination, and coextrusion of polymers such as LDPE, PLA, etc., in the past decade. Gallic acid functions by oxidizing with the formation of hydrogen peroxide, quinones, and semiquinones in an alkaline environment and is therefore an efficient oxygen scavenger. However, a base, mostly an inorganic compound, is always required to create an alkaline medium for the effective functioning of GA in the packaging material. For instance, K_2CO_3 is used as base by Ahn et al. LDPE-GA nanocomposite as mentioned in Section 3.1.2 [73,109]. Fasihnia et al. developed novel active polypropylene-based packaging films containing different concentrations of sorbic acid (SA), using extrusion molding. Increasing the SA concentration in films increased the antimicrobial properties of the films. The resultant films not only exhibited antimicrobial properties but also improved the mechanical properties and the barrier properties. The tensile strength and elongation at break of the prepared antimicrobial films are represented in Figure 14a,b [121].

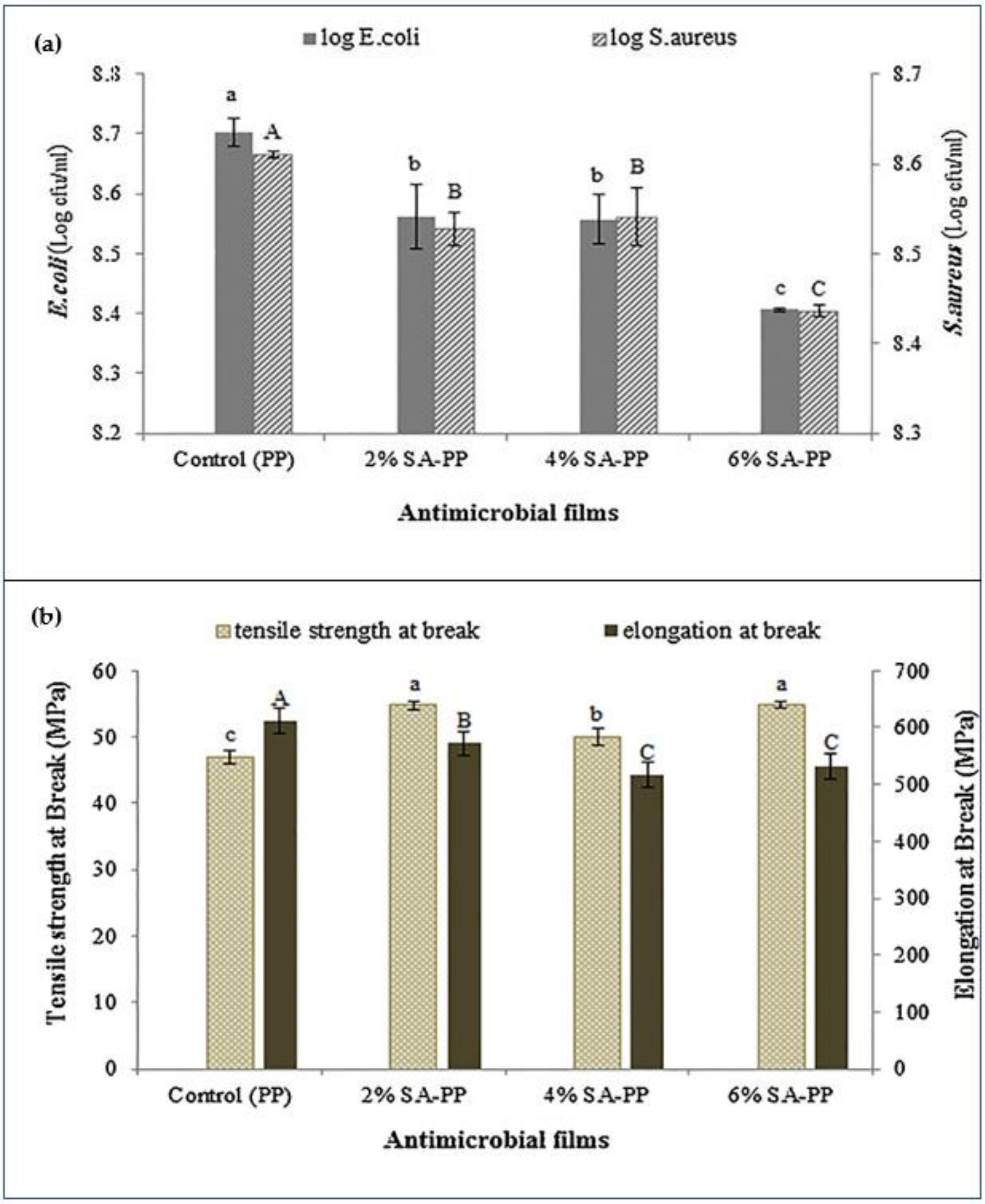

Figure 14. (**a**) Effect of different concentrations of SA on antimicrobial effects (**b**) mechanical properties of SA-PP films. * Small and capital letters represent a significant difference between samples for tensile strength at break (T) and elongation at break (E), respectively ($P < 0.05$). Reproduced from ref. [121] with permission from Elsevier. 2018.

Bacteriocins, such as nisin, have been proposed by many authors for antimicrobial food packaging. Colak et al. prepared nisin-incorporated films by extrusion, blowing, or heat pressing. Nisin-containing films prepared from nisin-containing pellets, either by heat pressing or extrusion blowing at 80 °C for 7 min, exhibited a lower antimicrobial activity as it had to withstand temperature and shear stress conditions during a thermomechanical process such as extrusion [122]. However, the residual antimicrobial activity was still significant and could be further improved by optimizing the formulation to limit inactivation.

Oyeoka et al. used cellulose nanocrystals (CNC) obtained from water hyacinth as reinforcement for PVA–gelatin nanocomposite. The resultant composite had a tensile strength in the range of 7–14 MPa and an elongation at break of 45–81%. Moreover, there was a considerable increase in the thermal stability of the film. In addition, the water vapor permeability was also observed to be decreased with the addition of cellulose nanocrystals. Therefor the PVA–gelatin–CNC film was established as a potential biodegradable food packaging material [123].

Agricultural waste materials, such as cocoa pod husk and sugarcane bagasse, both of which are wastes from the chocolate industry and the sugar industry, respectively, was exploited to make biodegradable packaging materials by Azmin et al. Fibers and cellulose were extracted from cocoa pod husk and sugarcane bagasse, respectively; they were integrated in various ratios and the resultant effects were studied. The film with a higher cellulose-to-fiber ratio showed excellent physicochemical properties. It exhibited optimal water vapor permeability and water vapor absorption for food packaging film as it aided to reduce mold formation [124].

Natural substances that work as antiviral agents, such as plant extracts and essential oils, are increasingly gaining popularity. The bioactive components in essential oils and natural extracts, particularly the polyphenols, are what give them their primary functionality. These substances are appropriate for consumption and generally recognized as safe without any harmful effects [92]. It has been observed that essential oils derived from plants such as oregano, artemisia, and salvia are particularly efficient against viruses such as HSV1, HSV2, and others. The viruses that cause dengue, tobacco mosaic virus, herpes, mumps, and HIV have been reported to be inhibited by essential oils such as anise, tea tree, eucalyptus, ginger, and artemisia. More importantly, some of these oils have been found to be effective against the coronavirus strain SARS-CoV-2, which is the cause of COVID-19 [125].

Polymers can be easily modified by blending, physical modification, chemical modification, and integration with active substances. Due to their biodegradability and outstanding sustained-release qualities, biopolymeric materials have also been seen as remarkable for food packaging, making them a beneficial alternative as base materials when combined with various active components. A wide variety of biopolymers have been combined with nanomaterials, essential oils, and plant extracts to produce antiviral packaging film and coatings. Biopolymers could be effectively utilized as carrier materials for active components with antiviral activities, thus paving a prospective future in sustainable anti-viral food packaging. It is also noteworthy that there are certain polyanionic biopolymers, such as sulfated polysaccharides (dextran sulfate, heparin, chondroitin poly sulfate, chitosan, hyaluronic acid), polysaccharides obtained from sea algae (carrageenan's, fucans, alginates, galactans, naviculans), and sea algae extract such as agar, that exhibit antiviral properties. All the above-mentioned polymers are increasingly being explored in the field of active packaging [91].

4. Detailed Overview of Extrusion Molding's Industrial Use for Active Food Packaging

Extrusion molding is the most promising polymer processing technique for any industrial-scale productions due to its several advantages such as flexibility, continuous operation, high-production volumes, reduced machine downtime, and compatibility with various raw materials. There are distinct types of extrusion process depending on the nature of the die type, number of screws, etc. Initially, synthetic polymers were introduced in the film extrusion market, but a successful extrusion of biopolymers into various molded parts contributed to an enormous growth in the current market. This review further analyses the extrusion processing of synthetic and biopolymers reinforced with active agents for packaging applications over the past few years.

4.1. Active Agents Incorporated into Synthetic Polymers

Zia et al. synthesized an active biocomposite film of LDPE and 5 wt. % curcumin by a melt extrusion and hot-pressing technique for active food packaging applications [64]. The extrusion of biocomposite films was carried out in a single-screw extruder of 20 mm diameter and an L/D (length-to-diameter) ratio of 20:1, a processing temperature of 145 °C, and a screw speed of 50 RPM throughout the process. The obtained polymer composite pellets were used to fabricate composite films using compression molding techniques. The active-composite homogeneous films showed better thermal stability, water vapor barrier, and antioxidant properties. Herniou-Julien et al. proposed an extrusion-processed packaging film made from carboxymethylated plantain flour/PS blends at a 50:50 ratio [126]. A twin-screw extruder with six heating zones, two feed zones, a profile temperature of 165 °C to 195 °C, and a screw rotating speed of 20 Hz were used to obtain the polymer composite pellets. Furthermore, the pellets were processed by thermo-molding under a hydraulic press to fabricate thermoplastic native plantain flour/PS-blended films. These films showed excellent antimicrobial activity, which is vital for both food packaging and biomedical implant applications.

Deng et al. developed a nanocomposite film by incorporating Ag NPs on a LDPE matrix using bolt-melt extrusion and a melt-compounding process [127]. A twin-screw extruder with a granulation temperature between 125 and 165 °C and a screw rotating speed of 25 RPM were used for the preparation of the film. The blown film temperatures were set at 145 °C, 165 °C, and 185 °C, while the host and tractor power were 2.2 kW and 0.75 kW, respectively. The acquired findings demonstrated that an LDPE/Ag NPs composite film may have a great potential for developing acid and antibacterial food packaging systems. Thanakkasaranee et al. developed polypropylene/sodium propionate (PP/SP) composite films via a melt-extrusion process to extend the shelf life of bread [20]. Firstly, a 20 wt. % masterbatch pellet of PP/SP at a 80/20 ratio was prepared using a lab-scale twin-screw extruder with a L/D ratio of 40:19 and a processing temperatures varying between 140 and 210 °C [128]. In a further step, the obtained pellets were processed again in the twin-screw extruder using the same processing conditions but using different wt. % of SP into the PP matrix. The films exhibited enhanced thermal, mechanical, antifungal, and antimicrobial properties that rendered them capable of extending the shelf life of bread.

4.2. Active Agents Incorporated into Biopolymers

The extrusion aided with supercritical fluids is an emerging processing technique to produce biopolymer foams. The dissolution of supercritical CO_2 into the melt polymer matrix acts as a plasticizer and decreases the processing temperature [129]. Darie-Niță et al. designed a novel ecofriendly packaging material using a twin-screw extruder (diameter screw = 35.6 mm, L/D = 32–48) for compounding PLA based biocomposites containing bioactive agents, such as rosehip seed oil encapsulated into chitosan and vitamin E [130]. The screw speed, temperature per zones, and pressure were significant technological processing parameters for obtaining pellets of PLA based composites. In line with the process, a pressure of 147 bars and a temperature of 175 °C were used, and the pellets were obtained as sheets and films using a laboratory press. In addition, a thermoforming process was performed with a prototype matrix using CAD software to obtain food trays. Ortiz-Barajas et al. prepared a novel green biocomposite by incorporating coffee husk flour (CHF) and torrefied coffee husk flour (TCHF) into a PLA matrix to reduce its ductility and toughness [131]. PLA with different wt. % of CHF and TCHF was melt-compounded in a twin-screw extruder (D = 25 mm, L/D = 24), using a profile temperature of 165–170–175–180 °C and a rotating speed of 40 RPM. Furthermore, the compounded pellets were injected molded into 4 mm pieces in a 270/75 meteor prior to characterization. The fabricated nanocomposites may find application in the field of rigid packaging and food contact disposables, where a high stiffness and low thermal resistance are required. Pal et al. synthesized a nanocomposite based on PHBV/PBAT blend organically modified nanoclays (0.6, 1.2, and 1.8 wt. %) using both compression molding and cast film extrusion techniques. A corotating twin-screw extruder (D = 27 mm, L/D ratio = 48:1), a temperature of 180 °C, and a speed of 100 RPM were used as operating parameters to produce polymer composite pellets. The pellets were further processed in a single-screw extruder (1.25 inch diameter) and an L/D ratio of 24:1, a processing temperature of 175 °C, and a screw speed of 30 RPM to fabricate cast-extruded films. In comparison with compression molding, the cast-extruded films exhibited better barrier properties due to the chain orientation during high-speed stretching. The nanocomposite film with 1.2% of nanofiller obtained through the cast film extrusion technique was found to have potential in the field of flexible packaging [132].

Mistretta et al. published a work on biocomposites based on two different biopolymers incorporated with two different modified nanoclays [133]. The preparation of three different nanocomposites with 5 wt.% nanofillers in a polymer matrix was carried out in a corotating twin-screw extruder with a temperature ranging from 145 °C to 180 °C and screw speeds of 205, 220, and 220 RPM. Afterwards, the nanocomposites were blown-molded in a single-screw extruder (D = 19 mm, L/D = 25), with a temperature profile of 120–170 °C, at a screw rotating speed of 80 RPM, a draw ratio of three and a blow-up ratio of two. The obtained blown films exhibited good mechanical properties.

5. Challenges and Future Scope

The challenging aspect of bulk synthetic methods is that the end-use activity of the active agents will always be inadequate since they involve hot-temperature processing settings, where the active components tend to deteriorate or degrade. Additionally, it may be complicated to obtain a thermally stable chemical for bulk active packaging production. Additional research is essential to develop a safe-by-design approach, such as encapsulation, to safeguard the active compounds.

Moreover, the bulk synthesis techniques do not guarantee the deposition of the active agents on the surface of the packing material, which is a crucial step for the antibacterial and antiviral capabilities to function effectively. Furthering this point, antiviral agents are anticipated to be present on the exterior surface of the packaging material because cross-infection of viruses occurs on the surface of the packaging material. Similarly, only when the active compounds are near the surface do they have the capability to stop microbial growth and scavenge free radicals, respectively. Additionally, another important property of food packaging films, for numerous reasons, is transparency. The addition of fillers to the bulk of the polymer might interfere with the transparency of the films. The development of stable NPs dispersion, which allows optimal transparency for the films is thus of great importance [134].

Active packaging has been receiving increasing attention in recent years, since it has been proven to be an effective strategy in maintaining the quality and prolonging the shelf life of food, thereby reducing food wastages. In addition, it also restricts the growth of microbes which may be potentially hazardous to human health. Adequate toxicological data are yet to be developed. The incorporation of nanoparticles as an active packaging approach is also under wide ambiguities. It is possible that the NPs may migrate to the food and get accumulated into the human body, subsequently causing severe damage to the cells. Hence, it is important to monitor the migration of particles. Moreover, a possible method to reduce this risk is the replacement with natural agents [78].

The regulations by the FDA and EFSA to commercialize active packaging are very stringent and hence it is difficult to commercialize them. Moreover, consumer acceptance and a lack of information are great challenges for the commercialization of active packaging. Researchers and industrialists could actively contribute to the effort of raising awareness through commercials or alternative routes [135].

To conclude, biodegradability and sustainability are key factors to be considered when discussing nanocomposite films. The development of completely biodegradable active packaging that can contribute to a reduced carbon footprint remains the biggest challenge of the current era.

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