Abstract: Special properties of the polymeric nanomaterials (nanoscale size, large surface area to mass ratio and high reactivity individualize them in food packaging materials. They can be processed in precisely engineered materials with multifunctional and bioactive activity. This review offers a general view on polymeric nanocomposites and nanocoatings including classification, preparation methods, properties and short methodology of characterization, applications, selected types of them used in food packaging field and their antimicrobial, antioxidant, biological, biocatalyst and so forth, functions.

Keywords: polymer; nanocomposites; nanocoatings; food packaging; risks; smart nanomaterials

1. Introduction

Nanoscience and nanotechnology applications to the agriculture, food sector and food safety are relatively recent compared with their use in cosmetics and personal care products (60%), paints and coatings, catalysts and lubricants, security printing, drug delivery and pharmaceuticals, medical therapeutics and diagnostics, energy production, molecular computing and structural materials [1–4]. Over $17.8 billion worldwide investment was made in 2010 for research and development in nanotechnology and this will grow to $3 trillion by 2020. Food packaging sector counts for ~50% market value for all nanotechnology-enabled products. Annual growth rate is 11.65%. Nanotechnology is mainly applied in extremely high gas barriers packaging materials with antimicrobial properties and in nanoencapsulants for the delivery of nutrients, flavours, or aromas [5,6].

According to regulation (EC) = No 1935/2004 a good packaging should have the following functions: “to protecting the food from dirt or dust, oxygen, light, pathogenic microorganisms, moisture and a variety of other destructive or harmful substances. Packaging must also be safe under its intended conditions of use, inert, cheap to be produced, lightweight, easy to dispose or to reuse, able to withstand extreme conditions during processing or filling, impervious to a host of environmental storage and transport conditions and resistant to physical abuse” [7].

Nanomaterials are applied in packaging and food safety in various forms such as: polymer nanocomposites with high barrier properties, intelligent packaging, nanocoatings, surface biocides, active packaging, silver nanoparticles as antimicrobial agents, nutrition and nutraceuticals, nanosensors and assays for the detection of food relevant analytes (gases, small organic molecules and food-borne pathogens) and bioplastics.

Main recent development areas in packaging field are:

(I) Improved packaging which offers improved mechanical properties as flexibility, enhanced barrier properties against water, gases, taint, durability, temperature/moisture stability, and so forth;

(II) Active/bioactive food packaging offers antimicrobial, antioxidant or biocatalytic functions. It can be obtained by the incorporation of active/bioactive compounds into matrices used in existing
packaging materials, or by the application of coatings with the mentioned functionality through physical or chemical surface modification. Active packaging is applied in food packaging, pharmaceuticals and consumer goods in order to improve shelf life, safety, or quality of packaged foods. Coating option is advantageous because the bulk properties of the packaging materials are preserved almost intact by using a minimum amount of active agent required to impart efficacy and therefore also cost is reduced.

(III) Smart/intelligent packaging as a promising area for active packaging coating is developed by manufacture of nano(bio)sensors which can indicate quality of foodstuffs, of nano(bio)switch to release preservatives and nano-coatings as antimicrobial, antifungal, antioxidant, barrier coatings, external stimuli responsive materials and self-cleaning food contact surfaces. Intelligent inks such as nanoparticles and reactive nanolayers allow analyte recognition at nanoscale. Printed labels are applied to indicate: temperature, time, pathogen, freshness, humidity, integrity [8]. Smart packaging may monitor various parameters such as: temperature, oxygen, pH, moisture and so forth [9–11] of packaged products.

2. Polymeric Nanocomposites

Polymeric nanocomposites are mainly obtained by dispersing of nanoscale filler into a polymeric matrix. Polymers commonly used in food packaging as either matrices or substrates for bioactive coatings are synthetic undegradable as low density and high density polyethylene (LDPE and HDPE), polypropylene (PP), polyethylene terephthalate (PET), ethylene vinyl alcohol (EVOH) copolymer, polyamide (PA), polystyrene (PS) and degradable ones as polyhydroxyalkanoates (polyhydroxybutyrate (PHB), poly(hydroxybutyrate-co-hydroxyvalerate) (PHBV)), poly(lactic acid) (PLA), polycaprolactone (PCL), polyvinyl alcohol (PVOH) and biopolymers as polysaccharides and proteins with critical issue on water resistance, migration and permeability and so forth. These properties may be improved by adding reinforcing compounds (nanofillers), forming bionanocomposites [12]. Because of the different characteristics, their application in food packaging is specific. For example, HDPE is used as milk bottles and bags, LDPE for trays and general-purpose containers, PP has a high melting point, being ideal for hot-fill liquids, films and microwaveable containers, while PET is clear, tough and has good gas and moisture barrier properties, so it is used for soft drink bottles, beverages and mineral waters, carbonated drinks and so forth [13].

While synthetic polymers generate huge waste quantity and have an environmental negative impact, by using degradable polymers these problems are avoid, because they are biocompatible and safe to use. However, most degradable polymers are in the research stage or their cost is high, some food packaging based on PLA (the cheapest bio-based material) and poly(butylene adipate-co-terephthalate) (PBAT) based packaging is used in Europe, Japan and North America [14,15].

Moreover, recently, a series of biodegradable nanocomposite films based on PBAT and reinforced with an organophilic layered double hydroxide OLDH (0.5–4 wt %) nanosheets were scale-up fabricated. Xie et al. reported such materials with “outstanding thermal, optical, mechanical and water vapour barrier properties a 37% reduction in haze and a 41.9% increase of tensile strain at break better than the pure PBAT film and commercial polyethylene packing materials” [16].

The active agents used in active packaging and coatings include antimicrobials, antioxidants and enzymes which control microbial growth, inhibit oxidative degradation reactions and offer a targeted biocatalysis that maintains food safety and quality and controls spoilage.

The most used nanofillers and nanoreinforcements are: clay montmorillonite (MMT) and kaolinite and silicate nanoplatelets (two-dimensional layers, which are 1 nm thick and several microns long), silica nanoparticles, carbon nanotubes, graphene nanosheets, silver, zinc oxide, titanium dioxide, copper and copper oxides, starch nanocrystals, cellulose nanofibres and nanowhiskers, chitosan and chitin whiskers and others. In respect with their geometry isodimensional nanoparticles have three nanometric external dimensions while nanotubes or whiskers are elongated structures with two
external dimensions on nanometre scale and the third is larger (Figure 1) [17–19]. Other classification is zero-dimensional, one-dimensional, two-dimensional and three-dimensional nanostructured materials [20]. Nanofibres may be also known as nanowire (electrically conducting nanofibre), nanotube (hallow nanofibre) and nanorods (solid nanofibre) [12].

![Diagram showing the external dimensions of nanoplate, nanofibre, and nanoparticle](image)

**Figure 1.** Representative images for nanofillers for nanocomposites. adapted from [17–19].

When only one dimension is in the nanometre range, the composites are known as polymer-layered silicate nanocomposites [21,22]. The role of nanofillers and nanoreinforcements in composites consists in the enhancement of the mechanical, thermal (glass transition, melting and degradation temperature) and barrier properties by increasing path length for gas diffusion, changes in surface wettability and hydrophobicity and so forth. For food packaging they may offer antimicrobial activity, oxygen scavengers, enzyme immobilization, biosensing and so forth. Nanocomposites usually represent significant changes in properties at low loads <5 wt % of nanofillers and <2% volume. Also, nanocomposites improve the stability of sensory properties, such as flavour, better maintenance of colour and texture, increased product stability through the food chain and less spoilage. It is well-known that the interfacial region in nanocomposites is extremely large, therefore the interaction of the polymer with the nanoparticles is strong and this will change the polymer mobility and relaxation dynamics, decreases chain mobility due to nanomodification and that means an increase in Tg [23].

Nanocomposites may improve both thermal and environmental dimensional stability. Two factors are considered responsible for improving the thermal stability in thermoplastic nanocomposites with
respect to the neat matrix: (i) the chemical composition and morphology of the nanocomposites is different from that of the pristine polymer; (ii) the thermal motion of the polymer molecules is restricted by the filler nanoparticles. Incorporation of nanofillers in thermoplastics usually led to a marked increase in the melt viscosity, especially in the range of low frequencies.

Several types of polymer nanocomposites are known depending on the nanofiller used as mentioned above. Examples include UV absorbers to prevent UV degradation of plastic polymers (e.g., nano-titanium dioxide, iron oxides, silica, alumina), titanium nitride (TiN) used to improve the strength of materials, nano-calcium carbonate-polymer composites, biodegradable starch and/or polylactic acid with various nanoclay composites, gas barrier coatings and so forth [24–28].

2.1. Preparation Methods

The preparation methods for polymer nanocomposites should assure a good dispersion of nanofiller into matrix to obtain intercalated or exfoliated structures [29–33]. The exfoliated nanocomposites are also classified as ordered and disordered exfoliations. Partial exfoliation is an intermediate morphology between intercalation and exfoliation. Significant variations in physical and mechanical properties of polymer nanocomposites are directly correlated with the differences in morphology [34].

There are two main strategies to obtain nanostructures and consequently polymer nanocomposites and nanocoatings—Table 1—so called “top down” or ex situ synthesis (attachment of nanoparticles to the polymer matrices prepared into different step) and “bottom up” or in situ synthesis methods (e.g., in situ polymerization, spin coating, casting) [35]. In the “top-down” approach the nanoparticles are produced in a separate step and then they are dispersed in polymer (direct mixing of the filler into a polymeric matrix, ball milling and application of severe plastic deformation, melt, or monomer solution which is then polymerized or nanostructures are generated by mechanical disintegration (milling) of the previous prepared material. In the “bottom-up” approach, the nanostructures are built up in a chemical process consisting in generation of nanoparticles inside polymer matrix or monomer polymerizing solution by chemical, thermal or photolytic decomposition of some precursors. Bottom-up approaches may be in gas-phase or in liquid phase such as: sol-gel processing, chemical syntheses, spraying, plasma or flame sputtering, spinning to make thin polymer fibres, chemical vapour deposition (CVD), laser pyrolysis, atomic or molecular condensation, electrodeposition, supercritical fluid synthesis, and so forth [36], while among the top-down techniques it is possible to include the energetic mechanical milling, sonication and so forth.

The preparation method determines both the concentration and distribution of the nanofillers and nanoreinforcements into the polymer [37].

The in-situ polymerization technique was widely used to obtain different kinds of nanocomposites such as those based on poly (vinyl acetate), nylon 6, in situ synthesis of polyurethanes PU in in dimethylformamide (DMF), emulsion polymerization of styrene in water and many others [38,39].

Solution mixing or solvent casting involves the vigorous stirring or ultrasonication of the nanoparticles in a polymer solution before casting in a mould and then evaporating the solvent. Both water and organic solvents can be used to prepare nanocomposites with either thermoplastics or thermosets. The removal of organic solvent after casting has environmental implications. The polarity of the solvent is a critical characteristic which influences the intercalation of the polymer into the space between the clay platelets. Nanocomposites are prepared by emulsion polymerization of acrylates in silica sols. By using this technique, it is possible to achieve a homogeneous distribution of silica nanoparticles into polymer at silica content up to 50% in the nanocomposites.
Table 1. Methods for preparation of polymer nanocomposites.

| Method                              | Method to Obtain Nanocomposites                                                                 | Results                                                                 |
|-------------------------------------|------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------|
| In situ polymerization:             | dispering fine nanofiller and nanoreinforcement in a monomer                                   | monomers interact with the nanofiller surface and form a uniform suspension |
| emulsion and miniemulsion polymerization |                                                                                               |                                                                         |
| Solution casting and latex method or solvent processing | 1. filler dispersal in the polymer solution  
2. solvent evaporation  
3. freeze-drying and hot-pressing  
4. freeze-drying, extruding and hot-pressing the mixture.  
5. surfactant addition  
6. grafting of long chains onto nanofiller surface | sandwiched multilayer structures forming of filler-rich layers  
 polymer polarity-based results  
The dispersion of nanoparticles in the nanocomposite film strongly depends on the processing technique and conditions |
| Direct addition/extruder Blending, melt processing Shear mixing | 1. addition of filler directly into the melted polymer  
2. blending either by (mechanical mixer and extruder) | target: to obtain uniform distribution of the nanofillers in a polymer matrix |
| Deposition or layer (LBL) assembly | Layer-by-layer deposition                                                                    | sequential substrate dipping in clay and polycation solutions were adopted to make the coating Multilayer films |
| Dispersion and chemical reaction    | UV-curing in presence of photo-initiator; casting, evaporating the solvent                    | cross-linked nanocomposites                                             |
| Electrospinning                    | development of electrospun nanofibers                                                        | nanofibres with different morphologies                                 |

At industrial scale of the extrusion or melt processing, the compounding of the components of a nanocomposite material is performed in a single or twin-screw extruder where the mixture of polymer and the nanofiller is a melt state. The shear and elongational stress applied with mixer during process help to break the filler agglomerates and uniformly dispersing them into the polymer matrix. As end products, films and other items can be formed from blend by profile injection moulding, extrusion, blow moulding. The intrinsic lack of thermal stability of many active/bioactive compounds which can be lost through degradation and evaporation during the heat transfer and high shear that also could degrade both the polymer and the nanofillers (as carbon nanotubes) limit the applicability of this preparation method. The homogeneous distribution of active agents into matrix is difficult. Processing at high shear or sonication techniques are used to deaggregate or exfoliate the clusters and to increase the surface area exposed to the polymer. Polymers able to interact with nanofillers give a good dispersion.

Shear mixing: Low-shear mixing or high-shear mixing can be used for incorporating solid nanoparticles into a liquid polymer. Under these conditions and if the nanoparticles are compatible with the selected polymer, the mixing will disrupt the nanoparticle aggregates and disperse the polymer matrix into the nanoparticle layers or onto the nanoparticle surfaces. The dispersion degree of the nanofiller and the filler/matrix interaction can be generally improved by (i) using surface-treated filler to reduce aggregation phenomena and (ii) incorporating a compatibilizer or a tensioactive agent within the polymer matrix (such as maleic anhydride grafted polypropylene).

LBL and electrospinning techniques are described in the nanocoatings section.

2.2. Types of Polymer Nanocomposites Used in Food Packaging

Some types of nanocomposites used in food packaging are given in Table 2 [12,33].

2.2.1. Montmorillonites (MMT) Containing Nanocomposites

The polymer–clay morphologies are classified in (1) tactoid, (2) intercalated and (3) exfoliated. In the tactoid structures due to the poor affinity of nanoclay with the polymer, the interlayer space of the clay gallery will not expand, the components do not mix each other and nanocomposites are not formed. In intercalated structures a moderate affinity between polymer and clay exists hence they are characterized by moderate expansion of the clay interlayer but the shape remains unchanged, polymer chains are able to penetrate the basal spacing of clay, mixing of components being homogeneous.
A high affinity between polymer and nanoclay promotes separation of the clay clusters into single sheets within the continuous polymer matrix resulting a homogeneous dispersion as the *exfoliated structures* which determine important changes in properties of the nanocomposites in respect with those of neat polymer.

Generally, MMT behaves as an effective reinforcement/filler, offering a high surface area and large aspect ratio. However, in many cases the compatibility with the matrix should be improved both by organophilization of the filler, the use of surfactants or compatibilizers. By these ways better exfoliated structure and better mechanical properties are achieved for nanocomposites. Clay layers constitute a barrier to gases and water, forcing them to follow a tortuous path, nanocomposites showing improved oxygen and water vapour barrier properties and some of them as Cloisire 93A, Cloisite 30B and Dellite High Pressure Sodium HPS offer also antimicrobial activity against both Gram-positive and Gram-negative bacteria, excepting fungus *Candida albicans* [40]. In many cases the mechanical properties are improved, glass transition and thermal degradation temperatures increase but some nanoclays decrease transparency of the films [12].
Table 2. Some examples of nanofillers intended to be used in nanocomposites for food packaging (for many examples see also recent reviews on this subject [41–44].

| Type of Nanofiller | Matrix | Preparation | Properties/Applications | Ref |
|-------------------|--------|-------------|-------------------------|-----|
| Organoclay        | LDPE and HDPE | melt mixing using PE grafted with maleic anhydride as compatibilizer-exfoliation | oxygen permeability of PE decreases gradually with the clay concentration, reaching a maximum reduction of ~30% for 15 wt % MMT; dynamic moduli increase showing pseudo solid-like behaviour at clay concentrations higher than 8 wt %. | [45] |
| Nanolayers of Nanoter™ from NanoBioMatters LTD Spain | PE | melt processing | very good barrier properties | [46] |
| 4% MMT | EPDM | melt processing | decreased N₂ permeability by 30% | [46] |
| Bentonite | PLA | solution casting | improve strength and modulus; decreased elongation at break | [46] |
| 5% MMT | PVOH | casting | 90% reduction in water permeability retaining optical clarity | [46] |
| MMT | proteins and polysaccharides | casting | 60% reduction in water permeability | [46] |
| 1.1%–4%–10% Various unmodified and organically modified MMT, Cloisite 25A, Nanoter™ | PLA, PCL, PHA, PHBV Strach | monolayer packaging | exfoliated and intercalated structure depending on MMT amount, Tensile strength of a chitosan film was enhanced and elongation-at-break decreased | [48] |
| MMT | chitosan films | solvent casting | exfoliated clay. | [48] |
| MMT | poly (ε-caprolactone) (PCL) | electrospinning | improved mechanical properties even elongation at break | [48] |
| Anionic sodium MMT exfoliated | cationic polyacrylamide on a PET substrate | Layer-by-layer (LbL) self-assembly multilayer film | oxygen transmission rate (OTR) decreased as a function of number of bilayers deposited, until a negligible value—below 0.005 cm³/(m² day atm)——for a 30-bilayer film, microwaveable and with a good optical transparency (higher than 90%), it was presented as a good candidate for aluminium foil replacement in food packaging. | [50] |
| 5% Clay ZnO stabilized with sodium carboxymethylcellulose | thermoplastic starch; gelatinized starch film glycerol plasticized-PEA starch | melt extruded | improve the mechanical strength of biopolymers, decreased water vapour permeability by using only 5% (w/w) of clays; the highest exfoliation and best improvement in mechanical properties, exfoliated clay. | [51,52] |
| Type of Nanofiller | Matrix | Preparation | Properties/Applications | Ref |
|-------------------|--------|-------------|-------------------------|-----|
| 1 wt % and 5 wt % of modified (surfactant-modified) and un-modified cellulose nanocrystals, | PLA | solvent casting method in the presence of surfactant | reductions of 34% in water permeability for the cast films with 1 wt % of surfactant modified-CNC; good oxygen barrier properties; the migration level of the studied nano-biocomposites was below the overall migration limits required by the current normative for food packaging materials in both non-polar and polar simulants. | [53] |
| Up to 3% cellulose nanocrystals CNCs | PLA | extrusion, twin-screw extruder | water vapour permeability decreased gradually with increasing addition of CNCs up to 3%; good oxygen barrier properties; enhanced barrier and mechanical properties | [54] |
| Cellulosic nanoparticles in chloroform and layered silicates; whiskers | PLA | dispersion in non-aqueous medium, casting; addition of PVOH | An improvement in storage modulus over the entire temperature range for both nanoreinforcements together with shifts in the tanδ peaks for both nanoreinforcements to higher temperatures; reduction in the oxygen permeability for the bentonite nanocomposite but not for the MCC nanocomposite. The amount of light being transmitted through the nanocomposites was reduced compared to pure PLA indicating that both nanoreinforcements were not fully exfoliated | [47,55] |
| Cellulose whiskers extracted from PEA hull fibres with different hydrolysis times, which resulted in different aspect ratios. | PEA starch matrix | | The composite produced by using the whiskers with the highest aspect ratio exhibited the highest thermomechanical properties, reduces the water sensitivity and keeps biodegradability; Tg increases; moisture resistance improved | [56,57] |
| Cellulose whiskers | PVOH | solution casting, water solvent | the modulus increased by orientation of reinforcement under magnetic field | [58] |
| Cellulose nanowhiskers | k/l carrageenan | casting | high crystallinity, enhanced water barrier of carrageenan | |
| Bacterial cellulose nanowhiskers | PLA | casting | improved barrier properties to gases and vapours, fully renewable biocomposites for biopackaging | [59] |
| Bacterial cellulose nanowhiskers | EVOH or PLA | electrospinning | increased thermal stability | |
| Bacterial cellulose nanowhiskers | EVOH | melt compounding | enhanced barrier and mechanical properties of EVOH | |
### Table 2. Cont.

| Type of Nanofiller | Matrix | Preparation | Properties/Applications | Ref |
|-------------------|--------|-------------|-------------------------|-----|
| 30 wt % of Straw cellulose whiskers | poly(styrene-co-butyl acrylate) latex film | freeze-drying and moulding a mixture of aqueous suspensions | modulus more than a thousand times higher than that of the bulk matrix | [60] |
| Aqueous suspensions of polysaccaride (cellulose, chitin or starch) nanocrystals, tunicin (the cellulose extracted from a tunicate-a sea animal) whiskers, wheat straw or sugar beet cellulose nanocrystals, potato starch nanocrystal and squid pen and Rifta tubes chitin whiskers | hydrophobic polymers as: styrene and butyl acrylate [poly(S-co-BuA)] poly(β-hydroxyoctanoate) (PHO) polyvinylchloride (PVC), waterborne epoxy, natural rubber (NR) and polyvinyl acetate (PVAc), poly(styrene-co-hexyl-acrylate) | dispersion of these nanocrystals in non-aqueous media is possible using surfactants or chemical grafting long chain surface chemical modification; mixing and casting the two aqueous suspensions, freeze-drying, extruding and hot pressing; mixture extrusion methods, miniemulsion polymerization | films; larger latex particle size results in higher mechanical properties | [30] |
| aqueous suspension of polysaccharide nanocrystals | hydrosoluble or hydrodispersible polymers as: reinforced starch, silk fibroin, poly(oxyethylene), polyvinyl alcohol, hydroxypropyl cellulose, carboxymethyl cellulose or soy protein isolate | mixing and casting the aqueous solutions, freeze-drying and hot-pressing | enhanced strength, elongation and Young’s modulus. The chemical grafting of the starch nanocrystals StNs did not affect positively the strength and elongation, because such a treatment inhibited the formation of physical interaction and increasing network density in nanocomposites | [61] |
| starch nanocrystals | waterborne polyurethane | solution casting; chemical grafting of starch nanocrystals | improved not only the tensile properties (tensile strength and elastic modulus) of the matrix but also its water resistance | [62,63] |
| Coating of cotton and tunicin whiskers by a surfactant phosphoric ester of polyoxyethylene (9)-nonyl phenyl ether leads to stable suspensions in toluene and cyclohexane or chloroform | atactic polypropylene, isotactic polypropylene, or (EVA) | dispersion in non-aqueous medium, casting | decreased mechanical properties | [64] |
| Chitin whiskers | protein isolate thermoplastics | solution-casting technique | improved chitosan films tensile strength until a whisker content of 2.96%, while higher increases of whiskers contents resulted in decreasing strength. Improved water resistance of the films. | [65] |
| chitosan–tripolyphosphate (CS–TPP) nanoparticles | hydroxypropyl methylcellulose (HPMC) films | solution-casting technique | improved mechanical and barrier properties of the films | [66] |
| carbon-based graphene, 20 to 60 nm in thickness and 0.5 to 25 µm in diameter, at 1 to 5 wt % loading | poly(methyl methacrylate) (PMMA) | dispersion at 30 °C by high speed shearing methods | heat resistant, high barrier nanocomposites promising in food packaging; increase the glass transition temperature of PMMA | [67] |
MMT containing nanocomposites show many advantages in respect of neat corresponding polymeric matrices; they are lighter, stronger, more heat-resistant, offer improved barrier against gases, moisture and volatiles materials, antimicrobial properties and so forth. They are produced by Nanocor Inc. (Arlington Heights, IL, USA) and Southern Clay Products, Inc. (Gonzales, TX, USA), Mitsubishi Gas Chemical (New York, NY, USA) and other units using as matrices Nylon-6, PE, PET and EVOH. Films, PET bottles and multilayer films from nanocomposites are obtained to prolong the shelf life of a variety processed meats, cheese, confectionery, cereals and boil-in-bag foods and so forth [8, 68, 69].

2.2.2. Bionanofibrils

Biopolymer nanofibrils with dimensions of angstrom to hundreds of nanometre scales arise from renewable resources, are widely available at low-cost, offering exceptional biocompatibility, biodegradability, flexibility and the availability of multiple reactive sites for introducing novel functionalities. Because of the natural origin and well-defined supramolecular assemblies and geometries they exhibit exceptional mechanical properties mainly a unique combination of strength and toughness. Their biological functions allow the interactions with the surrounding environment performing a variety of specific functions in living systems and also serving as building blocks stabilized by non-covalent interactions in material science. The nanofibrillar biopolymers are potential candidates for high-performance and functional bionanocomposites as strong, sustainable, stimuli responsive and biocompatible materials for a wide range of applications such as environmental, energy, food packaging, optical and biomedical [70, 71]. The combination of biological and synthetic components frequently shows synergistic effects because of strong interfacial interactions that significantly enhance the structural performance and facilitate added functionalities of nanocomposites. In some bionanocomposites, novel synthetic nanoparticles (graphene, carbon nanotubes, mineral nanoparticles, metallic nanoparticles and so forth) were efficiently combined with biological components to achieve superior electrical and thermal conductivity, controlled gas barrier properties, complex actuation and unique optical properties [72]. The biopolymer nanofibrils as cellulose nanofibrils (CNF), chitin nanofibrils (ChNF), silk nanofibrils (SNF) and collagen nanofibrils (CoNF) are most abundant nanofibrils in nature. The nanocellulose and silk nanofibrils, are representatives of classes of polysaccharides and polypeptides [73].

Both top-down and bottom-up strategies have been developed to exfoliate and regenerate bionanofibrils.

Nanocellulose is a term referring to nano-structured cellulose. This may be either cellulose nanocrystal (CNC), cellulose nanofibers (CNF) also called microfibrillated cellulose, or bacterial nanocellulose, which refers to nano-structured cellulose produced by bacteria (BC). They are renewable abundant raw materials derived from wood and plants. As biodegradable fibre-reinforcement for polymeric bionanocomposites, they also offer excellent tensile properties, non-toxicity, high thermal conductivity and optical transparency as indispensable requirements for advanced food packaging.

Cellulose-based nanoreinforcements (as cellulose microfibrils or nanofibers and microcrystalline cellulose). Cellulose microcrystals may contain also amorphous areas. Nanofibres have nanosized diameters (dimension range of 2–20 nm, depending on the bionanofibril origin) and lengths in the micrometre range. Whiskers are crystalline parts and are known as nanocrystals, nanorods, or rod like cellulose microcrystals with lengths ranging from 500 nm up to 1–2 μm and about 8–20 nm or less in diameter and high aspect ratios. Microcrystalline cellulose has 200–400 nm in length and an aspect ratio of about 10 [12]. Their dimensions affect the properties of nanocomposites. Nanocellulose can be extracted via enzymatic pre-treatments, tempo oxidation and chemical extraction, while CNC are extracted generally via acid hydrolysis with sulfuric acid [74–76].

Polysaccharide nanoparticles as aqueous suspensions hydrosoluble (or at least hydrodispersible) or latex-form polymers are obtained. The dispersion of nanocrystals into non-aqueous media is also possible using surfactants or chemical grafting. These are other possibilities for processing of the nanocomposites. The surface of the polysaccharide nanocrystals is covered with reactive hydroxyl
groups, which provide the possibility of their extensive chemical modification using grafting agents bearing a reactive end group and a long compatibilizing tail [30]. The surface chemical modification of the cellulose biofibres leads to improved interfacial adhesion between the fibres and the matrix, resulting in enhanced mechanical properties and thermal stability. CNC coatings are also transparent, nontoxic and sustainable. CNCs are highly crystalline and easily dispersed in water, therefore the structure can be controlled to eliminate free volume and to improve barrier properties of the materials. They offer to coatings a higher density and packing that reduces diffusion pathways and drastically improves oxygen, carbon dioxide and water vapour permeability properties which are similar with those of EVOH commercial food packaging material. Their use is also associated with biodegradability and sustainability [77]. Bacterial cellulose (BC) nanofibrils randomly-oriented as web-like form show full potential as reinforcement. To orient the nanofibrils a controlled stretching of BC hydrogel was performed by Rahman and Netravali [78,79]. They obtained a BC-reinforced soy protein isolate (SPI) by vacuum-assisted SPI resin impregnation into BC hydrogel and then stretching the resin impregnated BC hydrogel. Aligned BC nanofibrils were produced by cultivating them inside polydimethylsiloxane (PDMS) tubes followed by wet-stretching. Due to higher BC nanofibrillar orientation, the stretched BC-SPI green composites showed significant improvement in their tensile properties. Cellulose nanofibrils were produced from commercial bleached cellulose pulps after 30 passages in a SuperMasscolloider Grinder (MASUKO SANGYO CO., Kawaguchi, Saitama, Japan), or using mechanical processes [80]. Films were prepared by a casting method. BC-reinforced PLA showed enhanced barrier and mechanical properties [81].

Hybrid nanocomposites, where two different nanoparticles CNC/metallic nanoparticles CNF/clay and CNC/clay) are incorporated into the polymer have been also obtained. [82] PLA-based nanocomposites with CNF, 1–5% nanocrystalline cellulose (CNC) and 1–5% nanoclay (Cloisite™ 30B) for food packaging use led to up to a 90% reduction in the oxygen transmission rate (OTR) and 76% reduction of water vapour transmission rate (WVTR), significant increase in thermomechanical resistance and increased crystallisation kinetics. [83,84] The incorporation of nanoparticles will increase the tortuosity within the material and that this increases barrier properties.

The corona treatment leads to the quality improvement of fabrics and composites. It was applied with good for surface modification and physical and mechanical properties of nanofibril containing films useful for printing and packaging materials such as eucalyptus and pinus nanofibril films [85]. After the corona discharge and subsequent exposure to oxygen from air hydroxyl, carbonyl and other functional groups are formed by breaking C–C bonds and interaction with active species from plasma (see below). After such treatment, the Eucalyptus nanofibril films showed increased tensile strength due to their higher crystalline index and nanofibril dimensions.

Chitin nanofibrils were directly extracted from crab shells through a green deprotonation-assisted liquid exfoliation procedure. By aqueous re-dispersibility after freezing/air/thermal drying, hybridization with other two-dimensional nanomaterials, (e.g., graphene and transitional metal dichalcogenides) was performed. Plasticized PLA with 1 and 5 wt % chitin nanocrystals (ChNC) nanocomposite after orientation, showed a ‘shish-kebab’ morphology in the drawn tapes. Singh et al. reported improved mechanical and thermal properties. The tensile strength increased and the elongation at break increased from 5% to 60% for the nanocomposite with 5 wt % ChNC and a draw ratio of 3 because of the synergistic effects of the ChNC in the nanocomposite and their alignment of the ChNC together with the polymer chains induced by the solid-state drawing [86].

Silk fibres. A variety of artificial spinning methods have been applied to produce regenerated SNFs. Ling et al. developed a bioinspired spinning method [87]. They prepared nematic silk microfibril solution, highly viscous and stable by partially dissolving silk fibres into micro-fibrils. The hierarchical structures in natural silks was maintained in solution which was spun into regenerated silk fibres by direct extrusion in the air. In this way, polymorphic and hierarchical regenerated silk fibres with physical properties beyond natural fibre construction were generated. By further functionalization
with a conductive silk/carbon nanotube coating, responsive materials to changes in humidity and temperature can be produced.

The following surface modifications were applied: Poly (ethylene glycol) PEG-grafted rod-like cellulose microcrystals [88], alkenyl succinic anhydride acylating the surface of cellulose nanocrystals, crab shell chitin whiskers [89], waxy maize starch nanocrystals [90] and tunicin whiskers used then to reinforce some plastics [91,92] their performance depending on type of matrix.

*Starch nanocrystals* show platelet morphology with thicknesses of 6–8 nm. Their incorporation lead to improve some properties of PVOH [93] and pullulan [94].

### 2.2.3. Other Types of Nanofillers

**Carbon nanotubes** (CNT). Tensile strength/modulus of PVOH [95], PP [96], PA [97] are improved by addition of CNTs.

**Silica nanoparticles** ($n$SiO$_2$) improve mechanical and/or barrier properties of PP [98], mainly when maleic anhydride grafted polypropylene (PP-g-MA) is used as a compatibilizer [99], of PVOH [100] or of starch matrix [101].

**Halloysite** (HAL) represents a class of natural, non-toxic, non-swelling silicates, stable even at very high temperatures and show a good encapsulation and release capacity for bioactive compounds (anticorrosion, antimicrobial, drugs, flame retardant, microcrack self-healing). They have a wide variety of applications including also as fillers and reinforcements for polymers. The HAL particles can adopt a variety of morphologies, as elongated tubules known as halloysite nanotubes (HNT), short tubular, spheroidal and platy particle shapes, the first one being the most common [102]. HAL can be incorporated into different polymers to obtain non-degradable and degradable nanocomposites with versatile properties some of them being attractive for potential uses in food packaging [103]. The HNT-incorporated polymer nanocomposites can be prepared by various processing routes such as melt blending, melt spinning, water-assisted extrusion process, methods involving hydrogen bonding and charge transfer mechanism, solution casting, co-coagulation or co-curing processes, in situ or emulsion polymerization techniques for nondegradable nanocomposites and solution casting, coagulation, electrospinning for HNT-containing degradable nanobiocomposites. HNTs containing nanocomposites exhibit remarkable mechanical performance and their properties can be tailored by HAL surface modification [104], by nanocomposites composition and by the preparation methods optimization. HAL nanofillers act as ethylene gas absorbers. This gas causes softening and aging of fruits and vegetables; limits the migration of spoilage-inducing gas molecules within the polymer matrix. Active food packaging materials as HNT/PE nanocomposite films showed higher ethylene scavenging capacity and OTR and WVTR than neat PE films. Due to their ethylene scavenging activity and good water vapour and oxygen barrier properties, the nanocomposite films slow down the ripening process of bananas and retain the firmness of tomatoes and also slowed down the weight loss of strawberries and aerobic bacterial growth on chicken surfaces. HNT/PE nanocomposite films contribute to food safety improving the quality and shelf life of fresh food products [105]. Starch/halloysite/nisin nanocomposite films inhibited activity of *Listeria monocytogenes*, *Clostridium perfringens* and *Staphylococcus aureus* in skimmed milk agar being active and useful barrier to control food contamination [106]. HNTs loaded with lysozyme, as nano-hybrid antimicrobial was incorporated into a poly (ε-caprolactone) (PCL) matrix at 10 wt % and then the films were submitted to a cold drawn process. The films exhibit a controlled release of lysozyme being for specific active packaging requirements [107].

**Graphene** as atomically thin carbon sheets improve physical properties of host polymers at extremely small loading. Nanocomposites containing graphene are obtained by top-down strategies starting from graphite oxide, solvent- and melt-based strategies [108]. Such nanocomposites offer extremely high barrier performance at even very low graphene loadings, which is interesting for food packaging [109].
Metallic nanoparticles incorporated into food contact polymeric matrices enhance mechanical and barrier properties, prevent the photodegradation of plastics and are effective antimicrobials (as salts, oxides and colloids, complexes) such as AgNP [110]. Copper, zinc and titanium NP are also useful in food safety and technology. Copper is an efficient sensor for humidity and titanium oxide has resistance to abrasion and UV-blocking performance [111].

Lignin nanoparticles were tested for their antioxidant, antimicrobial activities and potential biological being effectively used as active agents towards different pathogen strains when is combined with PVA, chitosan CH, natural polymers and so forth [112,113].

Multifunctional nanocomposites contain usually a mixture of micro- and nanostructured materials such as essential oils, natural extracts and metal nanoparticles with antimicrobial/antioxidant agents/biological functions and they are also interesting for food contact materials.

2.2.4. Bioplastics–Biopackaging

Increased use of the synthetic packaging materials (as films, bottles, trays and so forth) has led to serious ecological problems due to their non-biodegradability and waste accumulation. Biopolymers derived from natural resources as plants (starch, cellulose and their derivatives, proteins), animal (proteins, polysaccharides) and microbial products, such as polyhydroxybutyrate have been extensively studied in the bio-based nanocomposites field [114] because of their good biocompatibility, degradability [115] and recyclability [116]. The starch-clay biodegradable nanocomposites were investigated for several applications including food packaging. Some restrictions are encountered on the use of biodegradable or natural polymers in food packaging since they have poor barriers and mechanical properties, high permeability to gases, such as oxygen and water vapour because of their hydrophilic nature with a few exceptions, such as caseinates, which show excellent barrier performance, even better than PET [117]. Nanoreinforcements can improve barrier properties and have a positive impact on the oxidation stability, thermal and mechanical characteristics and eventually bionanocomposites show the good biodegradability comparing with conventional polymeric matrices. Polymer cross-linking and graft copolymerization of natural polymers with synthetic monomers/polymers are other alternatives of promising values in biodegradable packaging. The complete replacement of synthetic polymers with degradable ones is almost impossible to achieve and even unnecessary, at least for specific applications the use of biodegradable polymers is desirable. No doubt, in the future biopackaging will be increasingly developed [46,118].

Protein-based nanocomposites. In commercial applications, the following animal derived proteins used are: casein, whey protein, collagen, egg white and fish myofibrillar protein. The plant-based proteins also under large scale application consideration include soybean protein, zein (corn protein) and wheat gluten. Compared with non-ionic polysaccharide films, protein films, due to their more polar nature and more linear (non-ring) structure and lower free volume offer better oxygen barrier properties and lower water vapour permeability [119]. The transparent films based on whey protein show good oxygen barrier and TiO$_2$ or ZnO were added to form nanocomposites with improved antimicrobial properties [120–122] used to fabricate food-grade, biodegradable packaging materials. Chen et al. and Yu et al. showed that the addition of small amounts (<1 wt %) of TiO$_2$ nanoparticles significantly increased the tensile properties of whey protein film (from 1.69 to 2.38 MPa). Soy protein nanocomposite films exhibited reduced water vapour permeability, improved elastic modulus and tensile strength compared with neat polymer [123,124]. Zein as biodegradable polymer is used in the food industry as a coating agent [125]. It is less water sensitive than other biopolymers but shows high water vapour permeability and low tensile strength when compared with commodity polymers. To ameliorate its inherent brittleness, plasticizers may be used.

2.2.5. Degradability and Recyclability of Nanocomposites

Bionanocomposites (BNC) can be recycled/valorised or treated together with other organic wastes in composting facilities and produce compost, as valuable soil conditioners and fertilizers
and so forth [126]. They are high-performance biodegradable materials, based on plant, animal and other natural materials, therefore these are safely decomposed into CO\textsubscript{2} consumed during plant photosynthesis, water and humus through the activity of microorganisms [127]. This behaviour refers to with BNC with degradable polymeric matrices like poly(lactic acid) (PLA), poly(butylene adipate-co-terephthalate) and thermoplastic starch which undergo degradation after various time period. Different biodegradation conditions can be considered: hydrolytic, composting, enzymatic, according to the final applications and the post-use of the new developed materials [128].

Combining the individual advantages of starch/synthetic or natural polymers and nanoparticles (cellulose nanocrystals, clay, TiO\textsubscript{2}, layered silicate and so forth) starch-based completely biodegradable materials with potential applications in food industry as edible films were prepared. [129].

The effect of the nanofillers on degradability and compostability of bioplastics depends on their type. PLA/Laponite biocomposites showed the greatest microbial attachment on the surface (biofilm is formed), while PLA/ organo-montmorillonite (OMMT) had the lowest biofilm formation because of the inhibitory effect of this NP during biodegradation test. Nanoclays influence the polymer bacterial degradation due to the affinity of the bacterium towards clay. The addition of nanoclays during composting process increases the PLA degradation rate due to the presence of hydroxyl groups from the silicate layers of these clays. As an example, due to the hydrophilic nature of nanocellulose, the cellulose nanocrystals (CNCs) increased the disintegrability rate of PLA.

PLA bio-nanocomposite films containing nanoclay with organo-modified (with methyl, tallow, bis-2-hydroxyethyl, quaternary ammonium montmorillonite), Halloysite nanotubes and Laponite® RD, MMT showed a significantly higher mineralization of the films in comparison to the pristine PLA, mainly attributed to the reduction in the PLA lag time. PLGA/CNT films were degraded by hydrolytic degradation [130]. CNTs insignificantly modifies the kinetics and the mechanism of the hydrolytic erosion with respect to the neat PLGA, while CNTs functionalized with carboxylic groups accelerated the hydrolytic degradation and the weight loss of the PLGA matrix of the nanocomposites.

MWCNTs reduce the biodegradation rate of PCL in the presence of \textit{P. aeruginosa}, systematically as the CNT loading increased from 0.1 to 10% \textit{w/w} [131].

### 3. Polymer Nano-Coatings in Food Packaging

A coating is defined as a coherent layer formed from a single or multiple applications of a coating material to a substrate. Nanocoatings are ultra thin layers on the nanoscale (<1–100 nm thick built-up onto surfaces [132,133]. Nanocoatings do not modify the surface topography, they do not fill in defects or make a smooth surface like a paint does, and they also do not stand up to abrasion and wear. They are used to impart a particular chemical or physical function(s) to a surface as gas-barrier coatings, hydrophilic/hydrophobic or oleophobic properties, improve corrosion resistance and enhance insulating or conductive properties [134].

Nanocoatings can be built up with thickness of one molecular or multiple molecular layers. Nanocoatings are applied to various substrates such as metals, glass, ceramics, polymers and so forth (Figure 2) [135,136]. Some nanocoatings are polymers, either polymerized in-situ or prior to application. “Smart coatings” are coatings with multifunctional additional functions some also assuring thermal insulation, controlled release of active ingredients or self-healing functions.

Additives are added to a coating material in very small quantities. They can modify a large variety of properties, for instance, flow behaviour, surface tension, gloss, structure, UV and weather resistance. Depending on the desired function, nanotechnology-based functional coatings uses some nanomaterials as in the case of antimicrobial coatings containing silver, titanium dioxide, zinc oxide, some organic bioactive agents as polysaccharides, proteins, spice and herb extracts as essential and vegetable oils, bacteriocins (ex: Nisaatin®, nisin, pediocins), organic acids for food packaging or hygienic surfaces. Nanomaterial-containing coatings offer high performance materials and better processing properties than conventional coatings (e.g., increased indentation resistance, high elasticity, fast drying, no expansion after contact with water, high water vapour permeability).
3.1. Types of Nanocoatings

Several types of nanocoatings are known in food packaging applications as: nanocoating inside package, outside package, sandwiched as a layer in laminated multilayer packaging films, polymer with nanocoating with high barrier properties, edible coatings and films on a wide variety of foods which serve as moisture, lipid and as gas barriers [137], vacuum deposited aluminium coatings on plastic films, coating of the surfaces of glass food and beverage containers (bottles, jars) with organosilanes, nanosurface biocides and so forth.

Nanosilica-coated films onto PET, Nylon and so forth, replace polyvinylidene fluoride (PVDF) coated films and oxide evaporated films, for processed meat products (beef meta, sausage, ham and so forth, fresh food like rare fish, sushi, dried fish and so forth, bakery, sandwiches, snack, candy, nut products with high fat) and so forth [28], offering oxygen and moisture barrier and aroma preservation increased self-life and decreased production cost, good printability and laminating machinability, are eco-friendly, no dioxines are formed during incineration, excellent mechanical and optical properties (retaining bulk properties of base film).

Nano surface biocides (using as nanoparticles: nanosilver as metallic Ag, AgNO3, ZnO, TiO2, MgO) are obtained by incorporation such nanomaterials with antimicrobial properties onto packaging surface. Such food contact nano surface containing biocides maintain the hygienic conditions when applied to reusable food containers such as boxes and crates and inside liners of refrigerators and freezers.

The most known coating technologies are immobilization using covalent (non-migratory) and non-covalent (migratory), layer-by-layer deposition, photografting chemistries and embedding for controlled release, schematically represented in Figure 2 [135–140].

![Figure 2. Summary of coating technologies (adapted from [135–140]).](image)

In coating technology which uses the embedded agents for controlled release, the active agent is intended to migrate to the packaged good (embedding, non-covalent immobilization, some layer-by-layer deposition techniques) while in non-migratory technologies, the active agent is intended to remain stable in the packaging matrix (in covalent immobilization, some layer-by-layer deposition techniques, photografting). Some techniques to prepare nanocoating are similar with those for nanocomposites obtaining, some are adapted and other are specific for this purpose. In some cases, the nanocoatings application required specialized equipment and complex procedures, such as, chemical vapour deposition or plasma spray techniques.
The active agents are expected to migrate and exert their specific antimicrobial, antioxidant, biocatalytic, or nutraceutical functions within a packaged food. Active compounds are incorporated into polymeric materials by extrusion/blending and pip-coating techniques or solution casting.

3.2. Coatings Procedures

3.2.1. Solution Casting

Solution casting consists of dissolving the polymer in a suitable solvent and simultaneously incorporating the active compound of interest, followed by pouring this mix solution onto an inert surface. By the solvent evaporation, the films with desired functionality (antimicrobial, antioxidant, pharmaceutical, biocatalytic and so forth) result. It is mainly used at laboratory scale and can be translated at industrial scale by coupling with a wet-coating station and roll-to-roll system [141]. However, it has some limitations both for practical and commercial application because the most of the interesting polymers used in food packaging dissolve only at high temperatures and in certain organic solvents [142], which will affect both the stability and effectiveness of many active/bioactive compounds of interest. Therefore, the incorporation of active compounds through solution casting has mainly applied when biodegradable polymers dissolved at milder temperatures, such as poly(lactic acid), poly(ethylene adipate-co-terephthalate) and cellulose derivatives, PVOH and so forth [143]. Butnaru et al. obtained films by casting and dried in a vacuum oven with controlled temperature using solutions of highly viscous chitosan from crab shells where food grade vegetable oils (clove, thyme and rosehip seeds oils) were incorporated were homogenized by ultrasonication [144].

3.2.2. Extrusion

In commercial extrusion, the active compounds with polymeric materials in melted state, in a single or twin screw extruder by heat transfer where are incorporated a blend is obtained from which films can be formed. It also has serious limitations due to the intrinsic lack of thermal stability of many active compounds as it was already mentioned above, which can be lost either through degradation and evaporation. During the heat transfer involved in these unit operations the homogeneous distribution of active agent into matrix is difficult. The active compound release is controlled by packaging material characteristics such as the degree of affinity between it and the matrix, morphology and porosity and also by medium temperature. Multilaminated system in which the layer that harbours the active compound is covered by an adjacent layer could act as a barrier slowing release rate. In such case the bulk properties as tensile and thermal are changed therefore the coating technique is preferred.

3.2.3. Sol-Gel Procedure

Sol-gel procedure is extensively used in obtaining of nano-based coatings. A viscous colloidal-sol is applied to a surface by dip, spray or spin coating processes onto surface. The thickness of the obtained layers varies from a few nanometres thick to 0.5 and 3 µm. The process occurs at low temperature, in a short time, is low energy consuming and more important without disruption of the structure or functionality of biocomplexes or organic aggregates, the nanocoating as a gel may exhibit a porous 3D network [145].

3.2.4. Spraying Solution with Compressor Gun

There several types of sparaying guns as manual and automatic spray guns with air compressors, etc. Manual spray guns are available in various configurations to suit a wide range of applications and processes. HVLP (high volume low pressure) gun offers the following advantages: the spraying is controllable, high transfer efficiency, can be used for a wide variety of materials, it is inexpensive to maintain because needs a reduced preparation and clean-up, is portable, the material consumption is reduced by 40%.
Their applications are: painting, food industry, pharmaceutical, dyestuff coating, oil, lubricating, rubber solution spray, textile spray, water based materials/paints, etc.

They are already applied on a large scale both by individuals and industrially.

3.2.5. Surface Immobilization

Surface immobilization of the bioactive compounds was performed for a wide range of inert hydrophobic packaging polymeric materials. Surface modification of polymers can be performed either by physical, chemical (wet) or biological methods. Physical methods are preferred over chemical techniques because they offer greater precision, ease of process control and environment friendliness. Classical physical methods for modifying polymer surfaces include flame and corona treatment, ultraviolet light, gamma-ray, ion-beam techniques, low-pressure plasma and laser treatment. Physical methods either modify the surface layer or an extraneous layer is deposited on the top of the existing material—coating. The main advantage of plasma treatments is that the modification is restricted to the uppermost layers of the substrate, thus not affecting the overall desirable bulk properties. To achieve approximately similar surface modification, gamma irradiation should apply only in mild controlled conditions [146,147].

The physical methods are widely used due to their easier industrial scalability, no liquid reagents of any kind are needed in their application, thus is avoided the accumulation and handling of harmful waste [148]. The main effect of the surface activation methods is the formation of reactive species on the polymer surface like oxygenated groups as carbonyl, hydroxyl and carboxylic acid groups or nitrogen containing groups depending on discharge gas used in plasma device or after air exposure. On activated polymer surface bioactive compound can be either covalent or non-covalent immobilized Figure 2. Non-covalent way is based on electrostatic interactions when substrate and bioactive compound show opposite net charges, while ligand–receptor interactions, like in the case of biotin–avidin [149] are specific for affinity immobilization.

Covalent attachment/conjugation of bioactive compounds to functionalized polymer surfaces is realized by: hydrophilic, bifunctional, and/or branched spacer molecules. The main advantage of covalent immobilization is high stability of the formed layer and the active compound does not migrate into the packaged food product to affect its quality and safety. Active agents can be covalently linked directly to the polymer surface or by use of a spacer or crosslinker, which either share a permanent covalent bond between the polymeric substrate and the bioactive compound, or promotes covalent bond formation between the activated substrate and the bioactive compound without forming part of that link (“zero-length” crosslinkers). It can also perform optimization of the surface functionalization by using a polyfunctional agent, increased number of functional groups, tethering a bioactive compound to a solid substrate via a spacer molecule, covalently attach a bioactive compound to the functionalized polymer surface via an intermediary. The immobilization technologies are potential versatile as once functional groups are introduced to the polymer surface, a range of bioactive agents (e.g., enzymes, peptides) can be immobilized through standard chemical or bioconjugation techniques [150].

Plasma and gamma rays assisted nanocoating and immobilization. Plasma treatment and gamma irradiation are energetic processing methods that create reactive spots to which either oxygen- or nitrogen containing groups can be implemented on surface and functional groups and radicals are created depending on the type of discharge gas/atmosphere used inside reactors. The energy levels of entities generated in cold plasma are comparable to the bond energies of organic compounds and thus can facilitate surface functionalization reactions. The extent of functionalization can be controlled by selecting the discharge parameters [139]. On polymer surfaces three main effects can be obtained depending on the treatment conditions: a cleaning effect, an increase of microroughness surface and functionalization. According to the literature data acidic surfaces are obtained by O2 and air plasma activation of inert surface of synthetic polymers [151] and amphoteric surfaces are obtained by N2 plasma activation [152,153], in all cases after exposure to air for the same period of time of about 1
min. Nitrogen containing functionalities originate from plasma treatment itself and also, very likely, from the post-reaction with the venting gas. The oxygen atoms are both in the form of alcohol (C–OH) or/and carbonyl (C=O) groups, epoxy groups and radicals, while the nitrogen atoms appear as amino (C–NH₂) groups. In order to develop new multifunctional active polymeric surfaces with special properties for food packaging applications based on inert polymer such as polyolefins or polylactic acid and polyalkanoates, the following solutions have been applied:

a. Activation of polymeric substrates by non-solvent, environment friendly methods by using of gamma-ionizing radiation or cold plasma gas discharge.

b. Stable layers have been deposited onto activated polymeric substrates using different coupling agents for covalent linking of active/bioactive formulations.

c. Selected bioactive compounds were: chitosan/chitin, lactoferrin, vitamin E, natural vegetable oils with high content of antioxidant compounds as phenols or flavonoids mixtures.

Covalent grafting of bioactive compounds onto inert polymeric surfaces occurs by a two-step procedure:

Step I. Polymeric surface activation.

Surface activation techniques are applied in order to introduce the desired type and quantity of reactive functional groups which are able then to covalently attach a bioactive compound. The polymeric films/papers were exposed both to corona and to high-frequency plasma (air or nitrogen were used as discharge gas). The most important feature of irradiated polymers is the possibility of grafting for certain structures, because the radical sites are available for coupling. γ-exposure of polymeric films/papers was carried out in an irradiation machine at various irradiation doses from 2–30 kGy absorbed in air, at room temperature. Surface functionalization because of implementation of polar groups and radicals onto substrate surface provides desired changes in physical properties of the substrate surface (e.g., wettability, improved adhesion and biocompatibility, interaction with surrounding media) [154]. Although physical adsorption may be useful in some applications, covalent immobilization provides the most stable controllable bonds, between the bioactive compound and the functionalized polymer surface [155]. Optima conditions of activation by each method or compound to be linked were established by varying the exposure parameters and determination of the dependence of the surface wettability and morphology on these [146,147,156–162].

Step II. Covalent bonding/grafting of bioactive compound onto activated polymeric surfaces.

After the corona, plasma discharge or γ-irradiation pre-treatment, the polymer surface was enriched with oxygen-containing groups, such as carboxyl, carbonyl, hydroxyl, ester groups and/or nitrogen containing groups. The covalent attachment between a polymeric surface and an active compound is achieved by formation of amide, ether, ester and thioester bonds, created between the hydroxyl, amine, imine, carboxylic acid and thiol groups of the active compounds of interest which may possess intrinsically (or are incorporated in their structure) and the functional groups created on the substrate [156,157,163,164]. After cold plasma/γ-ray exposure the polymeric films/fibres/papers were removed from the treatment chamber and then immersed into the bioactive compound solution (chitosan (CHT), grape seed oil, clove oil, etc.). The dipping/immersion, spreading or electrospinning/electrospraying of such solution onto activated surface lead to coat of the activated surface. For covalent bonding of CHT or other bioactive compounds onto activated surfaces, the Ethyl-3-[3-dimethylaminopropyl] carbodiimide hydrochloride) (EDC), -N-hydroxysuccinimide (NHS) or 1′-Carbonyldiimidazole (CDI) coupling agents were used.

Comparing various methods of chitosan deposition onto cold plasma and γ-irradiation activated PE surface it was established that for the same concentration of the chitosan solution the most efficient method was the immersion in respect with homogeneity of surface and thickness of deposited layer but the electrospinning appeared to be more versatile method, because it allows a more precise control of the chitosan content deposited onto the surface by varying the deposition time.
Attenuated Total Reflectance Fourier Transform Infrared spectroscopy (ATR-FTIR), X-ray photoelectron spectroscopy (XPS) and potentiometric titration proved CHT presence on the PE surface and also new bonds are evidenced mainly amide groups or ester groups because of interaction of –NH₂ or –OH groups of CHT with carboxyl group implemented on PE or PLA surface by radiation activation of surface. Other reactions were also possible because of the high reactivity of the active species created by plasma exposure/gamma irradiation and the functional groups of chitosan [157,165]. Chitosan coating improved the oxygen barrier properties of PE (Oxygen Transmission Rate (OTR) of PE decreased 3 times being of 1066 mL/(m²·day) while OTR of the uncoated PE is 3833.36 mL/(m²·day)). The potentiometric and polyelectrolyte titrations, zeta potential determination showed that some amount of chitosan desorbed faster from the surface until equilibrium was reached and also that the grafted chitosan layer was more stable than the physically adsorbed one. In the case of grafting, a thin chitosan layer was irreversibly immobilized on the PE surface. The obtained materials combine the antibacterial, antifungal, bioadhesivity, biocompatibility, biodegradability of chitosan [146,150,156,157,163–167] with the biological functions and antioxidative activity of vitamin E. Vitamin E is also known for its activity to prevent cell membrane damage by inhibiting peroxidation of membrane phospholipids and disrupting free radical chain reactions induced by formation of lipid peroxides [168].

The pH responsiveness was evidenced by contact angle measurements using buffered solutions with pH varying in the 2–11 range and it appears by sudden switching from hydrophilic to hydrophobic surface at critical pH ≈ 6. The contact angle of the polyethylene surface remains constant over the entire studied pH range (Figure 3).

Figure 3. Contact angle (θ) versus pH titration curves and derivative curves of dθ/dpH (insert) for chitosan/vitamin E-coated PE films adapted from [157].

Also, vegetable oils (clove oil, argan oil, thyme oil, tea tree oil and so forth) and combinations chitosan/vegetable oils have been tested to combine antimicrobial activity of CHT with those of vegetable oils and their antioxidant, biological function and nutrition [169]. They were covalently immobilized both on the activated substrate of PE and PLA and the results indicated their synergism in preventing microbial growth on fresh crude cheese, beef meat, poultry minced meat and fresh apple juice [136,140,146]. Both plasma activation and γ-irradiation have great influence on the antimicrobial activity being known that they are relatively simple and quite safe microbial sterilization techniques that are utilized in a variety of applications for their low operating costs and non-polluting capabilities.
In the case of lactoferrin immobilization it was established that gamma irradiated samples showed higher activities than those nitrogen plasma activated [150].

Lignocellulosic materials usually display a very low microbial resistance and microbial contaminations might be an additional issue to be taken into account. Conferring antibacterial activity to lignocellulose-based products may represent a main functional property which is useful not only for advanced food packaging [113] but also for textile applications. This can be realized by incorporation of aldehydes, epoxy, carboxylic acids and so forth [160,170] followed by attachment of some phenolic structures which can react at different extents with plasma/γ-irradiated activated surfaces and therefore they will be grafted on the lignocellulosic material surface to develop covalently bound antimicrobial products. The cellulose/chitin mixture and kraft paper were modified using different types of plasma: air, oxygen, nitrogen and argon activation followed by reaction with various phenolic compounds such as p-a-hydroxybenzoic cid (HBA), galic acid (GA) eugenol (Eu) and grape seed oil (GO) and rosehip seed oil (RO) and it was found efficient for inhibiting growth of microorganisms onto fresh crude cheese and beef meat. [160,171]. The antimicrobial activity was increased up to 100%. The rosehip seeds oil imparted the best antimicrobial properties to cellulose/chitin mix substrate. As functionalizable substrate is a biodegradable polymer and surface treatment was realized by physical methods of activation (cold plasma and gamma irradiation in mild conditions), the obtaining of the materials with desired surface properties avoided the harmful environmental concerns.

3.2.6. Wet Methods

Wet Methods involve both corrosive liquids to which the polymer substrates are directly exposed, like piranha solution (dissolved hydrogen peroxide and sulfuric acid), combined sodium hydroxide and sulfuric acid, chromic acid, potassium permanganate and nitric acid [172] and graft copolymerization. The first method has not a wide applicability but graft copolymerization received a wide scientific and applicability interest.

3.2.7. Photografting

Photografting method is a free radicals photografting procedure which occurs onto a polymer surface exposed to UV light in the 315–400 nm range in the presence of photoinitiators (e.g., benzophenone, anthraquinone, thioxantone, phenyl azide, polymers, curcumin) and monomers which usually bear ketone groups [173]. The active agent can be directly incorporated during photografting, or by its subsequent immobilization after grafting of a polymer chain with reactive functional groups (e.g., acrylic acid).

3.2.8. Biological Methods

Biological methods consist in: pre-adsorption of proteins, drug, enzyme immobilization, cell seeding and pre-clotting [174].

3.2.9. Chemical Vapour Deposition (CVD)

In typical CVD, the substrate is exposed to one or more volatile precursors, which react and/or decompose on the substrate surface to produce the desired deposit [175]. Diamond-like carbon (DLC) has been investigated as coating materials for industrial applications due to its outstanding characteristics such as high hardness, wear resistance, chemical inertness and biological compatibility. The demand for polymeric materials has also been increasing and highly functionalized polymers are much desired for wider applications to the production materials ranging from biomaterials to eco-friendly materials. In order to modify the polymers for highly-functionalized and highly biocompatible materials, DLC can be effectively nanocoated on polymeric materials, especially on polymeric surfaces through CVD methods. By nanocoating such DLC, a new type of polymer/DLC nanocomposite could be established for the use in biomedical devices and food packaging.
3.2.10. Atomic Layer Deposition (ALD) Method

VTT Technical Research Centre of Finland developed a fully recyclable nanocoating for food and pharmaceuticals [176] which is thin, light and air-tight, conformal and pinhole-free coating which follows the contours of the coated material, with excellent gas permeation resistance for packaging materials by ALD method. These thin bio-based packaging materials have gas permeability properties similar to those of existing dry food packages and pharmaceutical blister packs protecting the products from humidity, drying or oxidation. ALD coating allows integrating different functions into the packaging material, such as prevent water, oxygen, humidity, fats and aromas from permeating the packaging and protect the surface from stains and bacterial growth. The ALD technology improves the humidity tolerance and performance of bio-polymers, reducing the need for oil-based plastics.

3.2.11. Layer-by-Layer Assembly

By layer-by-layer assembly deposition can prepare active packaging coatings by the incorporation of active agents either between layers or within the structure of an individual polyelectrolyte [177]. Onto a polymeric activated substrate can be deposited by mutual attraction of polyelectrolytes with opposite charges or even by covalently attached of a polyelectrolyte such as proteins, polysaccharides, synthetic polymers of successive alternate layers [135,178]. Deposition can be accomplished either by submersion of the substrate into polyelectrolyte solutions or by spraying of solutions onto the substrate. The depositions are the presence optimized by adjusting the pH of their solutions for a full protonation or deprotonation, by maximizing of charge [179]. Between layers can be either only electrostatic interactions [180], and/or covalent bonds through the use of crosslinkers. The number of deposited layers is limited by a saturation state characterized by a thickness and stability of the system [181,182]. Jokar et al. produced coatings by the layer-by-layer deposition method. LDPE films were ultrasonically washed with acetone, functionalised in dilute aqueous solution of polyethylenimine for 10 min and sequentially dipped into anionic silver colloid dispersions containing PEG-capped silver NPs or cationic chitosan for 10 min. Silver particles were 18–32 nm and 22–30 nm in size in melt-blended and coated composites, respectively and their migration in simulated media as water, 10% ethanol, 3% acetic acid and apple juice depends on silver concentration and temperature [183]. Covalently bonded multi-layered films were assembled also using the LBL techniques by using polymers bearing functional groups capable of reacting with one another or with a bi-functional agent (diamines, diimides or dialdehydes). Covalent cross-linking increased the modulus and stability of the films.

3.2.12. Ultrasonic Nozzle Systems for Nanotechnology Coating Applications

Sono-Tek ultrasonic nozzles are suitable to depositing precision nanotechnology coatings for spray applications in research as well as production volume spray processes [184]. Uniform nanolayers of solutions onto any size or width substrate (including moving webs of material) are deposited and nano-suspensions are homogenously dispersed the onto a substrate, including suspensions that tend to agglomerate easily which are continuously break due to the mechanical vibration of the nozzle which is much efficient than air spraying. Sono-Tek systems employ the ultrasonic nozzle technology which enables to be easily scaled up from R&D to high volume production.

3.2.13. Plasma Nano-Coating of Beverage Cans

Interior and possibly even exterior coating of the aluminium cans and tubes is required in the food industry because the direct contact between the product and the packaging can lead to aluminium corrosion and the food could spoil. For example, the pasteurization increases corrosive impact on packaging. PlasmaPlus® coating technique uses the plasma jets deposit micro-fine glass-like nano-coats which form a highly effective protective film on the packaging with minimum material usage. Plasma coats provide a perfect quality imprinting [185]. Nobile et al. [186] produced the coating in polyethylene
oxide on the surface of PE film by plasma-based vapour deposition. Transmission electron microscopy (TEM) imaging revealed AgNPs about 90 nm in size deposited on the films. The migration of silver ions from nanosilver coatings onto PE films studied by immersion in distilled water, acidified malt extract broth and apple juice at 44 °C for 5 days. It was found that the silver content in the solutions was the highest in the distilled water simulant (1–1.9 mg/kg), with lower concentrations in the malt extract broth and apple juice (0.2–0.38 mg/kg).

3.2.14. Electrospinning/Electrospraying

Electrospinning/electrospraying has recently gained much attention because of its versatility in processing a wide range of polymer and biopolymer materials. It has the ability to produce fibre/particle diameters within the submicron and nano range using electric field which cannot be achieved by using conventional-generating technologies. Nanofibers have wide applications in industry such as food packaging coatings, composite materials, carbon nano tubes, inorganic fibres and tissue scaffolds, filtration, medical, membranes and so forth [187]. Electrospinning has been used to create a well-dispersed “concentrate” or master batch that will act as a carrier of well dispersed nanoparticles. It is an electro-hydrodynamic process, comprising electrospraying and electrospinning techniques which produces nanostructured fibre-based and particle-based materials both in laboratory and industrial scale. The devices used for the mono-axial and co-axial electrospinning/electrospraying method is presented in Figure 4.

![Figure 4. Representative experimental set-up of the uniaxial (a): (1) pump; (2) syringe; (3) collector; (4) high direct voltage (0 to 30 kV) power supply; or coaxial (b) electrospinning device used for immobilization of vegetable oil into chitosan and bioactive layer deposition onto polymeric activated substrate adapted from [146]; Vasile et al. (2016).](image)

In monoaxial electrospinning the device consists of a direct current high voltage supply, a metal plate collector sustaining the polymeric substrate, a pump and a syringe oriented perpendicularly to the metal plate with the low diameter needle (Figure 4a). A high direct voltage (0 to 30 kV) between the metal plate and the syringe needle is applied. The polymer solution is extruded through the needle tip by the syringe pump at a constant flow rate. At the point of ejection (the needle tip), is created a polymer jet because of the electric charge repulsion outgoing the solution surface tension. Based on electrostatic field between nozzle (needle tip) and collector, the dry polymer or solution are collected on the surface of collector screen. On the collector a very thin polymer layer is deposited, whose morphology as nanofibres or nanoparticles, depends on rheological properties of the solution [156] and composition of electrospinnable solutions [157,188]. This device has some disadvantages such as drying which can be controlled by the distance between nozzle and collector.

In co-axial electrospinning two syringes are used one of them being provided with a co-axial needle oriented with the needle perpendicular to the metal plate. It offers the possibility of depositing a bioactive layer/coating containing two bioactive compounds onto activated surface achieving the
encapsulation of less stable or liquid compound (as vegetable oils) into a polymeric one so core-shell morphology is obtained which can increase the coating functionality and protection of the labile bioactive component and also the use of nanomaterials in other technology. Encapsulation of the vegetable oils in chitosan was achieved by coaxial electrospinning method and immediately a coating of the nanoparticles/nanofibres was deposited onto polymeric substrate [146,189]. This technique may also be used with one of the two syringes with the polymeric solution and the other one with the same solvent able to dissolve the polymeric matrix. This approach is to improve the processability, being particularly interesting to scale up the electrospinning technique from lab scale to the industrial sector.

Electrospun fibres have a very high specific surface and porosity and they are able to encapsulate active substances. A wide range of applications are known for such fibres as improvement of physico-chemical and functional properties of biopolymer based materials by means of a controlled release of active compounds or by enhancing the dispersion of nano-additives into the biopolymer matrices. The nano encapsulation/entrapment can reduce the amount of active ingredients needed to obtain certain functionality and also their controlled release [158,188,190]. Nanofiber-based systems for antimicrobial food packaging and food contact surface applications contain antimicrobial fibre-base mats as coating of the packaging material, improve their activity in maintaining an optimal effect during the food storage period. Furthermore, the high surface to volume ratio of electrospun mats offer an efficient and prolonged delivery of loaded bioactive compounds.

An antimicrobial active multilayer system was obtained from a commercial polyhydroxyalkanoate substrate (PHA) and an electrospun PHA coating with in situ-stabilized silver nanoparticles (AgNPs) with satisfactory thermal, mechanical, barrier and antibacterial properties. It reduced the bacterial population of *Salmonella enterica* below the detection limits at very low silver loading of 0.002 ± 0.0005 wt %. Also, polyactic acid (PLA)/Silver-NP/Vitamin E bionanocomposite has been prepared by electrospinning and they showed a good antimicrobial activity against both gram positive and gram-negative bacteria [190]. As a result, this method provides an innovative route to generate fully renewable and biodegradable antimicrobial materials for food packages and food contact surfaces [191]. The choice of the manufacturing process depends on specific application requirements of the coating. As an example, the percent reduction against the fungus *A. Nigro* after 14 days, for the three multilayer samples coated with AgNP/polyethylene nanocomposites with the silver nanocomposite layer of AgNO₃ suspension (black) all at 1.0 wt % of silver content depends on the coating method, the most efficient being spraying one which gave a reduction of more than 70% while laminated and casting method reduction were of 20% and 45%, respectively [192].

4. Applications

Nanocomposites and nanocoatings applications in food packaging depend both on the properties of matrices/substrates and activity of ingredients. Nanoclay composites (usually montmorillonites) are used as flexible and rigid food packaging because of their excellent barrier characteristics in packaging of processed meats, cheese, confectionery, cereals and boil-in-the bag foods, items obtained by extrusion-coating process together with the paperboard are useful for fruit juice and dairy products and the beer and carbonated drinks bottles are manufactured by co-extrusion processes. For example, the PET bottles contain nanocore and nylon beer bottles with nanoclays show improved barrier characteristics. The active agents functions include antimicrobial, antifungal, antioxidant, biocatalyst, external stimuli responsiveness, additives that absorb undesirable component from food such as ethylene, moisture and odour and so forth. They are incorporated into matrix or coating to enhance the quality and shelf life of the food and are released in a controllable manner, the procedure being much efficient then direct addition into the food because they may react with other food components and loss their activity or affect food sensorial characteristics.

There are many formulations including such antimicrobials, antioxidants and biocatalysts, some of them being summarized in Tables 3 and 4.
| Active Agent | Substrate or Matrix | Technique | Characteristics/Observations                                                                 | Ref. |
|-------------|-------------------|-----------|---------------------------------------------------------------------------------------------|------|
| Essential oils; adhesion promoters (e.g., acrylic or vinyl resins or nitrocellulose) and fixatives | common packaging materials | different coating or spraying | controlled release | 193 |
| Bacteriocins (ex: Nisaplin® nisin, pediocins); spice and herb extracts; Organic acids, microencapsulated nisin | oleyl caprolactone, alginate, crosslinked chitosan/cellulose nanocrystal | crosslinking reaction under γ-irradiation | nanocellulose/PCL and alginate/cellulose nanocystal based edible films and ready-to-eat meat | 194 |
| Silver nanoparticles AgNP | poly(3-hydroxybutyrate-co-3-hydroxyvalerate) | extrusion/blending | sustained release of antimicrobial silver ions in food applications | 195 |
| Silver | poly(l-lactide) | melt-compounding | significant inhibition of microbial growth; migration rates below values reported by international imposed limits | 196 |
| AgNP/peptide/cellulose nanocrystals | PLA | solvent casting | the composite showed its biodegradation extent of 69.94% (after 90 days), offering good biodegradability for use as a material for the production of degradable plastic bags. The ageing, hydrolytic degradation and biodegradation of PLA-based films could be tailored by Ag kaolinite incorporation | 197 |
| AgNP/kaolinite | PLA and poly(butylene adipate-co-terephthalate) | blow films | | 198 |
| AgNPs | multilayer films of PHBV3 and electrospun fibres | compression-moulding, 180 °C and 1.8 MPa for 5 min; coated with PHBVs and PHBVs/AgNP ultrathin fibre mats produced by electrospinning followed by an annealing step; electrospun coating (~0.71 ± 0.01 mg/cm²) | multilayer materials for food packaging and food contact surface applications; efficient antimicrobial materials; bactericidal effect against *Salmonella enterica* | 191 |
| AgNP | PVOH | mixing a colloidal solution | improved thermal properties, enhancing stability and increasing Tg. | 199 |
| 2 wt % Ag-NPs | polyamide 6 | thermal reduction of silver ions during the melt processing of a PAs/silver acetate mixture | effective against E. coli | 200,201 |
| TiO₂/Ag grafted with γ-aminopropyltriethoxysilane | PVC | mixing | good antibacterial properties by photocatalytic bacterial inactivation | 202 |
| nano-Ag 35%, nano-TiO₂ 40%, kaolin 25% (30%) | PE | high-speed mixer; extruded by a twin-screw extruder and then film was obtained | Ag-NPs retarded the senescence of jujube, a Chinese fruit. | 203 |
| ZnO/Cu/Ag | PLA | melt processing | Antimicrobial materials | 189 |
Table 3. Cont.

| Active Agent | Substrate or Matrix | Technique | Characteristics/Observations | Ref. |
|--------------|---------------------|-----------|------------------------------|------|
| **Antimicrobials** | | | high performance nanocomposites with improved thermal, mechanical and antibacterial properties against both Gram-negative *E. coli* and Gram-positive *S. Aureus* of PHBV. Reduced water uptake and water vapour permeability; lower migration level in both non-polar and polar simulants because of increased crystallinity and improved interfacial adhesion. Great potential applications in the fields of food, beverage packaging and disposable overwrap films. | [204] |
| cellulose nanocrystal/silver nanohybrids bifunctional nanofillers—10 wt % CNC-Ag | poly(3-hydroxybutyrate-co-3-hydroxyvalerate) | solution casting | controlled release, total inhibition against *Aspergillus* flavus and *niger* and *Penicillium roqueforti* and *Penicillium expansum* | [205] |
| 30 µm thick coating containing 2–6% cinnamon essential oil | PP | spreading | controlled release, total inhibition against *Aspergillus* flavus and *niger* and *Penicillium roqueforti* and *Penicillium expansum* | [205] |
| 4% thyme and oregano essential oils | corona treated LDPE | ionizing treatment and directly extrusion | controlled release, inhibit *Escherichia coli* 0157:H7, *Salmonella Typhimurium* and *Listeria monocytogenes*, changes in barrier properties | [206] |
| Organic-inorganic hybrid coatings, polyvinyl alcohol with improved water resistance | poly(ethylene terephthalate) and oriented polypropylene | sol-gel technique condensation of hydroxylated monomers and polymers into a network | multilayer materials for packaging applications | [207] |
| Antifungal agent natamycin was embedded in a tetraethyl orthosilicate/EVOH gel | plasma treated PLA films | sol-gel | antimicrobial coatings; controlled release; inhibit mould growth on cheese stored for 30 days | [208] |
| Nanosilver or chitosan | LDPE | melt-blended and layered deposited silver | silver ion migration from the nanocomposites into the food simulants and apple juice was less than the cytotoxicity-level concentration (10 mg kg$^{-1}$) in all cases over 30 days | [209] |
| Antimicrobial photocatalysts (e.g., TiO$_2$) | PLA multi-layered hybrid coatings | sol-gel technique | Controlled release, antimicrobial | [210] |
| Polydiacetylene liposomes containing cinnamaldehyde as liposome-encapsulated cinnamaldehyde | amine-functionalized silane monolayer on piranha treated glass or amine-functionalized PLA films | nanoencapsulation and immobilization of cinnamaldehyde | Controlled release, efficient against *Bacillus cereus* | [211] |
| Sorbic acid and/or lauric arginate ester and chitosan and nisin | PLA or corona treated PLA | directly coated with the solutions, or treated with solution-coated polylactic acid (PLA) films | 2–3 logarithmic reductions of *Listeria innocua* (2–3 logarithmic reductions), *Listeria monocytogenes* and *Salmonella Typhimurium* negative effect on CO$_2$ gas barrier properties. There was no significant difference in the effectiveness of antimicrobial films versus the coatings. Antimicrobial packaging may be used alone, or in combination with flash pasteurization, in preventing foodborne illness due to post processing contamination of ready-to-eat meat products. | [212,213] |
Table 3. Cont.

| Active Agent | Substrate or Matrix | Technique | Characteristics/Observations | Ref. |
|--------------|---------------------|-----------|------------------------------|------|
| Peptide nisin entrapped in polyethylene oxide brushes grown on silane modified silicon wafers which protected nisin. | polyethylene oxide | entrapment | inhibition of Gram positive bacterium *Pediococcus pentosaceous* over a period of seven days | [214] |
| Pullulan powder was rendered cationic by reaction with an amine terminated silane as 3-aminopropyltrimethoxysilane | antimicrobial pullulan | immobilization | inhibits *Staphylococcus aureus* and *Escherichia coli* | [215] |
| Enzyme lysozyme covalently attached onto UV-ozone treated EVOH films immobilization via carbodiimide chemistry | covalently attached onto UV-ozone treated EVOH films | immobilization via carbodiimide chemistry | inhibits *Listeria monocytogenes* | [216] |
| (3-Bromopropyl)triphenylphosphonium functionalized with a quaternary phosphonium compound, (3-bromopropyl) triphenylphosphonium immobilization by azide-alkyne “click” reaction | poly(butylene adipate-co-terephthalate) | immobilization by azide-alkyne “click” reaction | inhibits *Escherichia coli* | [217] |
| SO₂ multi-layered film made of PA and PE was subjected to atmospheric plasma treatment (Ar, Na₂O and SO₂) on the PA side of the films | immobilization | inhibits *Escherichia coli* (82%), *Staphylococcus aureus* (86%), *Listeria monocytogenes* (63%), *Bacillus subtilis* (79%) and *Candida albicans* (75%) | [218] |
| Chitosan (polycation) and κ-carrageenan (polyanion) aminated PET layer-by-layer assembly improved gas barrier properties | aminated PET | layer-by-layer assembly | improved gas barrier properties | [219,220] |
| Lysozyme: κ-carrageenan alternated with two layers of the antimicrobial enzyme lysozyme | amine-functionalized PET films | layer-by-layer assembly | improved oxygen and water vapour permeability | [221] |
Table 4. Formulations including antioxidants and biocatalysts as bioactive compounds intended to use in food packaging.

| Antioxidants | | | |
| --- | --- | --- | --- |
| Citrus oil | plasma treated PET trays | spray deposition of citrus oil in methanol | controlled release; antioxidant activity with cooked turkey meat and retained activity after six months of storage [222,223] |
| Rosemary extract | LDPE plastic wrap or a polymeric carrier | applied direct onto LDPE plastic wrap or with a polymeric carrier | controlled release; 0.45 mg rosemary cm$^{-2}$ [224] |
| α-Tocopherol | paperboard using a vinyl acetate-ethylene copolymer as a carrier for controlled release | solvent casting coating at a concentration of 3% | antimicrobial and antioxidant coating; controlled release [225] |
| gallic acid | chitosan | immobilization by carbodiimide assisted reaction | reduced oxidation of peanuts [226] |
| Metal oxide coatings | Aluminium oxide or silicon oxide | biaxially oriented polypropylene and polyethylene terephthalate film substrates | reactive evaporation using an industrial high-speed vacuum deposition technique ‘boat-type’ roll-to-roll metallizer | transparent barrier coatings based on aluminium oxide or silicon oxide fulfill requirements such as product visibility, microwaveability or retortability reduce oxygen diffusion [227,228] |
| Tannic acid and poly(allylamine hydrochloride) | glass slides | layer-by-layer assembly | the number of bilayers increases in overall scavenging activity [229] |
| Caffeic acid | polypropylene packaging materials coating | photografting | prevent oxidative degradation of ascorbic acid in orange juice [230] |
| Acrylic acid | metal chelating active packaging coatings PP films, PP-g-PAA | photografting | prevent lipid oxidation in food emulsions [231–233] |
| Hydroxamic acid photografted polyhydroxamate chelators Plant-derived phenolic compounds, metal chelating PP | in situ polymerization of a mixture of catechol and catechin and oxidative polymerization with laccase and in alkaline saline and photografting | surface adhesion properties upon polymerization; non-migratory iron chelating active packaging material biomimetic iron chelating active packaging material, inhibit oxidation of food [234–236] |
| Lignosulfonate | Alginate | Solution casting | Antioxidant and UV protective films [113] |

| Biocatalysts | | | |
| --- | --- | --- | --- |
| Lactase blended into polyethylene oxide nanofibers | oxygen scavenging | electrospinning-enzymes or other active agents are incorporated into polymer nanofibers | controlled release, retained up to 93% of free enzyme activity [237,238] |
| Lactase | attachment of lactase to polyethylene films; | immobilization β-galactosidase bound to amine-functionalized PE films by a dialdehyde tether; polyethylene glycol tether size influences the attachment | reduce milk lactose in package; retained activity of immobilized lactase [239,240] |
| Lactase conjugated to nanomaterials | lactase immobilization onto nanostructures | lactase was attached to carboxylic acid functionalized magnetic nanoparticles 18 nm, 50 nm and 200 nm in diameter using carbodiimide chemistry. | retained activity of immobilized lactase; reducing the particle size of magnetic nanoparticles can increase the activity retention of conjugated lactase [241] |
| Lactase and polyethylenamine, glutaraldehyde | lactase covalently bound to low-density polyethylene | layer-by-layer assembly | more enzyme is immobilised but diffusion is difficult [242] |
Table 4. Cont.

| Enzyme Type                      | Preparation/Immobilization                                                                 | Function                                                                 | Reference(s)   |
|----------------------------------|---------------------------------------------------------------------------------------------|--------------------------------------------------------------------------|-----------------|
| Glucose oxidase                  | electrospun polyvinyl acetate/chitosan/tea extract fibres electrospinning                    | reduce oxygen in packaged foods                                           | [243]           |
| Glucose oxidase                  | chitosan LbL films                                                                        | biosensors                                                               | [244]           |
| Oxalate oxidase, oxygen-reducing enzymes in coatings and films for active packaging | extrusion-coated liner of polypropylene on top of the coating, entrapment in a latex polymer matrix | protective packaging gas-carbon dioxide; oxygen scavenging in active packaging; retained catalytic activity through entrapment in a latex polymer matrix | [245]           |
| Laccase-catalysed reduction of oxygen | it was possible to use lignin derivatives as substrates for the enzymatic reaction. laccase-catalysed reaction created a polymeric network by cross-linking of lignin-based entities, | resulted in increased stiffness and water-resistance of biopolymer films | [238]           |
| Catalase                         | layered haemoglobin, PS Immobilization                                                     | create a physical and chemical protective barrier                       | [229,246]       |
| Fungal naringinase               | cross-linking naringinase to polyvinyl alcohol and alginate                                | immobilization                                                          | [247,248]       |
| Protease, trypsin and endoproteinases | PP, PVOH and PS photografting, carboimide chemistry -covalently couple enzymes (via amine groups) to carboxylic acid groups poly(ethylene) glycol methacrylate and 4-vinyl-2,2-dimethylazolactone | antibody analysis in enzyme reactors                                     | [249]           |
| Hydrolase urease                 | photografted polytetrafluoroethylene                                                         | remove urea from beverages and foods                                      | [250]           |
| Glucose oxidase catalase for oxygen scavenging activity | low-density polyethylene and paper board multilaminate or combinations of LDPE, PP and PLA industrial lamination | scaled-up production in tetra pack pilot plan, scavenge oxygen to improve food shelf life | [251]           |
| Polysiloxane-based healing agents | acrylate matrix polymer coatings coaxial electrospinning                                     | self-healing polymer coating systems                                      | [252]           |
4.1. Antimicrobial/Antibacterial

Nanomaterials are more and more used to target bacteria in textile industry, marine transport, medicine and food packaging as antibacterial coatings and other materials [253]. Antimicrobial packaging role is to control the growth of pathogenic and/or spoilage microorganisms in packaged products. The diminishing and control bacterial colonization by the modification of the surfaces can be achieved [254]. As antimicrobial agents, essential oils, organic acids, peptides, enzymes and biopolymers are applied and nanoparticles like AgNP, MgO, CuO, Cu, ZnO, Cd selenide/telluride, chitosan, carbon nanotubes are used. Antimicrobial plant extracts from many plants and fruits such as thyme, clove and tea tree, rosemary oil or powder [169], sea buckthorn (Hippophaë rhamnoides L.) leaves and inner bark of pine trees (Pinus silvestris) [255] used in food packaging provide a healthy alternative. They contain aromatic and phenolic compounds that are responsible for their antibacterial properties and antioxidant activities. They can be applied as components in chitosan films or nanofibres obtained by electrospinning deposited on PLA [256]. Such essential or cold press oils exhibited selective antibacterial and/or antifungal effect both as a solvent extract and as a coating against three food spoilage fungi—Fusarium graminearum, Penicillium corylophilum and Aspergillus brasiliensis—and three potential pathogenic food bacteria as Staphylococcus aureus, Escherichia coli and Listeria monocytogenes and also against Pseudomonas aeruginosa.

TiO₂ and ZnO are non-toxic and approved by FDA as GRAS. TiO₂ nanoparticles exhibiting bactericidal and fungicidal effect against Salmonella choleraesuis, Vibrio parahaemoliticus, Staphylococcus aureus, Diaporthe actinide and Penicilium expansum. It was ultrasonically dispersed ethylene-vinyl alcohol copolymer films to obtain active packaging. It showed excellent bactericidal property under UV light [257]. Because of their very small dimensions, the nanomaterials are able to attach many biological molecules, therefore showing a greater efficiency [258]. ZnO is efficient both against Gram-positive and Gram-negative bacteria. NanoZnO coated films exhibit antimicrobial effects against L. Monocytes and S. Enteritis.

Have been proposed several mechanisms for the antimicrobial activity of nanoparticles as: directly interactions with microbial cells and interruption of the trans-membrane electron transfer, disrupting/penetrating the cell envelope, oxidizing cell components or producing secondary products as reactive oxygen species (ROS) or dissolved heavy metal ions. Secondary processes also can occur. For example, the antibacterial activity of silver ion is reduced by the protein rich food because it can bind the cysteine, methionine, lysine and arginine [259]. Nanosilver antimicrobial activity is explained by adhesion to the cell surface, degrading lipopolysaccharides and damaging the membranes, largely increasing permeability, by penetration inside bacterial cell, damaging DNA [260] and releasing antimicrobial Ag⁺ ions by AgNPs dissolution which then bind to electron donor groups in biological molecules containing sulphur, oxygen or nitrogen [261]. Silver ions can be released to destroy food spoilage. They show also a high temperature stability and low volatility. Nanosilver is useful as coatings component where the antimicrobial action occurs at the surface as on containers, mugs, dishes, cutlery, fridges, chopping boards and so forth [262]. It was found effective against numerous species of bacteria including E. Coli, Enterococcus faecalis, Staphylococcus aureus and Epidermidis, Vibrio cholera, Pseudomonas aeruginosa and putida and fluorescens and oleovorans, Shigella flexneri, Bacillus anthracis and subtilis and Cereus, Proteus mirabilis, Salmonella enterica typhmurmium, Micrococcus luteus, Listeria monocytogenes and Klebsiella pneumoniae [1,263] some of them presenting resistance to other potent chemical antimicrobials. Migration studies for nanosilver containing PE composites or coatings [264] in different simulants as malt broth, apple juice, distilled water and 10% ethanol showed good results.

The NanoBioMatters highly efficient antimicrobial product and BactiBlock® technology are based on silver-functionalized nanoclay. MgO and ZnO nanoparticles could provide cheap, safe alternative to expensive nano-sized silver as a heavy metal not suitable for human contact. The combinations of α—tocopherol with nisin or chitosan as coating or biocomposites confer both antimicrobial and antioxidative properties [136,140,225].
Antimicrobial activity of the chitosan and engineered nanoparticles is explained by several mechanisms including interactions between positively charged chitosan and negatively charged cell membranes, increased membrane permeability and rupture and leakage of intracellular material. They are ineffective at pH values above 6 because of the absence of protonated amino groups [265]. Another two antimicrobial mechanisms as chelation of trace metals by chitosan, inhibiting enzyme activities and, in fungal cells, penetration through the cell wall and membranes to bind DNA and inhibit RNA synthesis were also proposed [167].

**Carbon nanotubes** also have antibacterial properties. They are efficient against *E. coli*, possibly because puncture microbial cells [266] but is possible to be cytotoxic to human cells, to skin and lungs in processing stages rather than for consumers, therefore their migration to food must be carefully controlled.

### 4.2. Antioxidant

Oxidative degradation of food products happens during transport and storage producing lipid rancidity, colour loss (e.g., oxidation of carotenoids, chlorophyll, anthocyanins) and vitamin degradation. The antioxidants (e.g., free radical scavengers, metal chelators, singlet oxygen quenchers, oxygen scavengers) are commonly incorporated in food packaging by blending with polymers during processing (mixing, extrusion) [267,268]. The antioxidant active packaging technologies include oxygen scavengers, manufactured as sachets or labels and by the development of migratory and non-migratory antioxidant coatings. In the first case is possible a controlled release of an antioxidant (migration is 20 times less than the legal limits for the European Union) and sometimes does not requiring direct contact with the food [269]. Non-migratory antioxidant coatings may also be applied by covalent immobilization by means of the functional groups on the surface of packaging materials and shows advantages that do not alter sensorial properties of the packaged food product [270].

### 4.3. Biocatalytic

Enzymes onto solid support materials provide biocatalytic coatings for active packaging by catalysing some reactions. Biocatalysts are used in ingredients production and breakdown of undesirable components which are harmful or may decrease product quality. Biocatalysts are very sensitive, therefore the immobilization method onto and into solid supports must preserve their thermostability, optima pH and solvent stability and usually so-called “in-package processing” is applied to avoid changes during processing, transport and storage. Antimicrobial enzymes (e.g., lysozyme) are incorporated into active packaging coatings via blending, non-covalent binding for controlled release and covalent immobilization [150,271,272]. Their compatibility with matrix can be achieved by surface functionalization and cross-linking techniques [273]. The thermostability and pH stability of the bound enzyme determines the success of the coating method.

### 4.4. Barrier Applications of Polymer Nanocomposites

A critical issue in food packaging is that of migration and permeability [170,274] to atmospheric gasses, water vapour, or substances contained within both in the food being packaged or even the packaging material itself. As examples, in packages for fresh fruits and vegetables high barriers to migration or gas diffusion are undesirable because their shelf-life depends on oxygen for sustained cellular respiration while the plastics for carbonated beverage containers must have high oxygen and carbon dioxide barriers to prevent oxidation and decarbonation of the beverage contents. Though polymers possess numerous advantages their major drawback is an inherent permeability to gasses and other small molecules. PET provides a good barrier to oxygen (6–8 nmol/ms GPa) while this is very low for HDPE (200–400 nmol/ms GPa). The situation is opposite in respect with barrier against water vapour [170]. Oxygen and carbon dioxide barriers are necessary for plastics used for carbonated beverage containers. EVOH exhibits excellent oxygen transmission rate (OTR) values under dry conditions but under very humid conditions (relative humidity > 75%) it can
possess OTR values more than an order of magnitude higher due to its swelling and plasticization in the presence of diffused water molecules [275]. Bio-derived polysaccharide (starch, chitosan, pullulan) based packaging show even larger dependence of their OTR on humidity level, which has severely limited their usefulness. Thermoplastic biopolymers like PLA or polycaprolactones (PCLs) have good tolerance to moisture [276]. Because of the tortuosity effect created by the presence of highly crystalline CNCs (1% CNC) in the PLA-based nanocomposites, which increased degree of crystallinity all barrier properties are significantly improved (WVP (lower $\sim 40\%$); OP $\sim 75\%$ than neat PLA films). PLA/CNC with 1% nanofiber showed also improved of elongation at break [277–279]. Because of this specific dependence, complex multilayer films (by co-extrusion) [280] or polymer blends and composites are often preferred [281]. A high oxygen barrier, water sensitive material like EVOH was sandwiched between two layers composed relatively hydrophobic polyethylene [172]. Multilayer films and polymer blending require the use of additional additives and adhesives that complicate their regulation by federal agencies and arise recycling difficulties. Polymer nanocomposites (PNCs) should solve most of the above-mentioned problems.

4.5. Stimuli Responsive Nanocomposites/Nanocoatings

Stimuli responsive nanocomposites/nanocoatings prepared using “stimuli-responsive, “smart,” “intelligent” or “environmentally sensitive” polymers [282–285]. These polymers respond to environmental changes by changing their conformation, solubility, hydrophilic/hydrophobic balance, reaction rate, swelling and release behaviour (for hydrogels) and molecular recognition. Their response to the external changes are reversible, “switching” may occur repeatedly and occurs in a narrow interval of stimuli variation. Responsive polymers have found applications as free chains dissolved in aqueous solutions, as covalently or noncovalently crosslinked hydrogels and immobilized adsorbed or surface-grafted onto solid surfaces [286]. Surfaces modified with stimuli-responsive polymers dynamically modify their physico-chemical properties in response to changes in their environmental conditions. Stimuli-responsive surfaces have been created by the immobilization of reversible thermally responsive elastin-like polypeptide, on a glass surface [287]. The distance-dependent colorimetric properties of gold nanoparticles, enable to determine the effect of different variables on the lower critical solution temperature (LCST) at the solid–water interface. A poly(ethyleneimine)-poly(dimethylsiloxane) mixed brush switched spontaneously from the hydrophilic state in water to the hydrophobic one in air, therefore materials show a poor adhesion in a changeable environment. The surface coatings fabricated from mixed poly (ethylene oxide) (PEO)–poly(dimethylsiloxane) brushes or from fluorinated nanoparticles were adaptive to liquid and vapour environments so that the surfaces were spontaneously transformed to non-sticky states in air and in water. Smart and self-healing coatings have been also prepared. Colloidal particles obtained by the emulsion copolymerization of acrylate and fluorinated acrylate monomers form stratified film morphologies in superhydrophobic surfaces [288]. Thermoresponsive poly(N-isopropylacrylamide)-based microgels and assemblies have a diverse range of applications for example, biosensing, smart coatings and so forth [289].

Sensory Packaging is a category of devices used in intelligent packaging as nanosensors to monitor and report on the condition of food, communicate the degradation of product or microbial contamination and give information on history of storage, avoiding inaccurate expiration date increasing security and food safety. It helps food industry and retailers to now if the food package has been opened or tampered. This could be achieved by using a nanocrystalline indicator in form of an oxygen intelligence ink printable on most surfaces. This ink contains an UV light activated nanocrystalline particles of a semiconductor (usually TiO$_2$) or nanophosphourus particles. These particles are white in daylight but will fluoresce when exposed to light of certain wavelengths. The colour pigments can be also used as micro-colour codes in packaging and labelling applications. The development of sensory packaging which monitor the conditions of pharmaceuticals and foods are those affected by changes in temperature, humidity and shock. Nanobarcodes developed by Nanoplex
are written into fluorescent microspheres by photobleaching. Coating on PET bottles will expand the packaging of sensitive juice or beer beverages.

5. Possible Risks

Consumers are hesitant to buy nanotechnology foods or food with nanotechnology packaging. However, some results suggest that nanotechnology packaging is more beneficial than nanotechnology foods. The main concern with the application of the nanotechnology in food packaging is related to the fact that the very small sizes of the nanoparticles have different chemical and physical properties in respect of macroscale materials and it is possible they could cause health problems. New packaging materials must have good barrier properties to oxygen, carbon dioxide, water vapour and flavour compounds. This controlled release packaging is another example of a nanomaterial application in active packaging. Nanoclays can be used as carriers for the active agents with high efficacy because it is highly dispersed in the polymeric matrix and, hence, exposed more efficiently to the substance on which it is required to act. Potential implications for consumer safety are migration of nanoparticles. They can enter into body through ingestion, inhalation or dermal contact leading to health effects of exposure to some insoluble, persistent nanoparticles. Such health effects are currently not known. Nanoparticles also migrate to foodstuffs with possible adverse effects on food quality. Other concern is with degradability of bio-polymers and formation of degradation products with possible adverse effects. Also, may appear potential environmental impacts of nano-polymer composites and some problems with end-of-life treatments as recycling, re-use and disposal. Detecting the migration of nanomaterials requires more sensitive analytical techniques due to the complexity of the nanomaterials and because they represent only a very small portion of the bulk food. Migration into food can cause both undesirable organoleptic changes (migration of TiO\textsubscript{2} into lipid matrix results in rancidity) and in some cases nanoparticles of bioactive compounds are intended to be released deliberately.

A considerable number of migration studies were found for nanosilver containing polymer composites or coatings. Overall the results from these studies suggest the production method of nanocomposites (e.g., incorporation or coating, surfactant modification), starting silver concentration, temperature, time and choice of contact medium are all factors which may have an effect on the extent of silver ion migration into food simulants. In general, the rate of migration increases when nanosilver is coated onto the food packaging material or surfactants are added, when the storage temperature and length of storage increases and the acidity of the contact medium increases. There appears to be a specific time of storage, after which a steady state release of silver is achieved. This is supported also by a repeat contact migration experiments, which found silver migration decreased considerably (by an order of magnitude) after first contact. Nevertheless, there is some evidence to suggest that if silver nanoparticles do migrate into food/food simulants, they would most likely dissolve quickly into ionic silver. The majority of the migration studies found for nanosilver food packaging composites have shown levels of migration of ionic silver into foods and food simulants below the European specific migration limit (SML) of 0.05 mg Ag/kg food, suggesting low consumer exposure and subsequently low risk of adverse effects. However, there are also several studies, in which migration exceeded this limit. This indicates that for new food packaging products containing nanosilver, the migration experiments should be conducted in each particular case. Migration of intact nanoparticles into food simulants is negligible, implying consumer exposure to these materials is likely low. This suggests there is low potential for safety issues related to the nanosize level of the materials incorporated into food packaging. If they migrate in nanoparticulate form, it would be anticipated at the resulting low concentration in food that many of the metal oxide nanoparticulates would likely dissolve into their ionic forms upon contact with acid foods or stomach acid. Theoretically, potential consumer exposure to nanomaterials incorporated into food packaging will appear if: they migrate into foodstuffs or drinks from the packaging, or if the nanocomposite polymers degrade and ‘dissolve’ into food or drinks. Migration can theoretically occur if nanoparticles desorb from the surface of the packaging material due to weak bonding at the surface (only really relevant for coatings), diffuse into foods as a
result of a concentration gradient, or dissolve resulting in ions released into food [209,290]. However, currently, there are no internationally protocols or standards concerning nanomaterials characterization or to assess their implications on the consumers health [291–293]

6. Commercial Level

The companies producing nanoreinforced food packaging materials are Color Matrix Corporation manufacturing a high barrier nylon multilayer bottles films; Mitsubishi Gas Chemical Comp. Nanocore producing NANO-N-MXD6 for PET bottles; Lanxess for Durethan KU2-2601; Honeywell polymer with Aegis NC and OX as coating PA6 on paperboard and coinjection PET bottles [33], NanoSealTM Barrier Coating and Bairicade XTMTM Barrier Coating (from NanoPack Inc, Wayne, PA, USA) described as a water based coating comprised of a master batch and a liquid dispersion of clay platelets ('nano' or particle size is not mentioned). The coating is applied to traditional packaging films to enhance gas barrier properties and is stated to be approved for indirect food contact (i.e., used with dry and moderately dry food applications).

Nanocor Inc. Developed Imperm® as multilayer PET bottle and sheets is used to improve barrier properties and Nylon MXD6 Nylon MXD6-Ultra Barrier System [294], Duretham® KU 2-2601 (LanXess GmbH, Cologne, Germany) nylon nanocomposites for films and paper coating designed for medium barrier applications, requiring excellent clarity; Aegis® (Honeywell, NJ, USA) a polymerized nanocomposite film incorporating an active oxygen scavengers and passive nanocomposite clay particles.

“Micro-pore-plugging” film as single nanolayer on PET, manufactured by Tera-Barrier, provides transparency and stretchability for applications in food, medical and other packaging markets. Coating of 400 nm is obtained by slot die and has WVTR (40 °C and 100% RH) of $5 \times 10^{-2}$ g/(m² day), transparency 86% (PET 87%) at 550 nm, stretchability > 5%, average roughness 10.3 nm. Sidel trade name used for less sensitive foods are a coating of about 200 nm thick obtained inside PET bottle wall by acetylene plasma.

Barrier films are manufactured by Clairiant and Nanocore from PP and respectively Nylon with organoclay for packaging or PET beer bottle.

Purdue University developed a large-scale manufacturing process that may change the way some grocery store foods are packaged. This new manufacturing process uses cellulose nanocrystals as advanced barrier coatings for food packaging. The Purdue manufacturing technique is a roll-to-roll manufacturing process using waterborne polymer systems being scalable [77]. By their studies it appreciated that food packaging is a growing billion-dollar market and overall predicted growth is expected to reach 6 percent by 2024. Advanced barrier coatings, which help to protect grocery items such as foods and beverages, are growing by as much as 45 percent each year.

7. Conclusion and Future Trends

The global trade of active food packaging was estimated to be around US $12,000,000,000.00 in 2017 [295]. The active food packaging market is dominated by oxygen scavenging and moisture absorption applications [296,297]. Consideration must also be given to requirements of different regulatory agencies, under the jurisdiction of the Food and Drug Administration (in the United States), the European Food Safety Authority (in the European Union), or for each country. Non-migratory technologies produced by either covalent immobilization, cross-linked layer-by-layer deposition, or some photografted coatings offer a potential regulatory benefit. Migration testing using standardized simulants (water, 3% acetic acid, 15% ethanol, olive oil, iso-octane and 95% ethanol) must be performed to quantify levels of migrants in packaged product systems [298]. A benefit to coatings over bulk material modification is that bulk material properties should remain intact. However, the influence of the coating on processability, thermomechanical properties, barrier properties and seal strength must be characterized [299]. Rigorous application tests must also be performed to ensure that neither material conversion steps nor end use result in delamination of active coatings. Many of the coatings
technologies have potential for scalability to roll-to-roll, high throughput coating operations. Finally, while incorporation of active agents and specialized packaging processes will indeed increase material cost, the opportunities for new products, enhanced safety and reduced waste of packaged goods highlight the potential for increasing product value through smart integration of active biodegradable packaging coatings.

Nanotechnology has the potential to generate new food products and new food packaging. Analyses of individual data showed that the importance of naturalness in food products and trust were significant factors influencing the perceived risk and the perceived benefit of nanotechnology foods and nanotechnology food packaging [300–303].

Nanotechnology has been found to be a promising technology for the food packaging industry. It has proven capabilities that are valuable in packaging foods, including improved barriers; mechanical, thermal and biodegradable properties; and applications in active and intelligent food packaging including anti-microbial agents and nanosensors, respectively. However, the use of nanocomposites in food packaging might be challenging due to the reduced particle size of nanomaterials and the fact that the chemical and physical characteristics of such tiny materials may be quite different from those of their macro-scale counterparts. Migration studies must be conducted to determine the amounts of nanomaterials released into the food matrices [292]. Nanoscale dimensions can increase significantly the physical interactions, physico-chemical and chemical interfaces in materials [304]. The morphologies obtained for the nanocomposites and the ability to modify the interfaces are essential to maximize the properties. Surface treatment and intensive in optima conditions mixing are key solutions determining the nanomaterials performance. The combinations between nanofillers/matrix and bioactive compounds allow wide possibilities of mechanical, thermal, optical, electrical, barrier properties and multifunctionality to create good food packaging materials. Coating technology has undergone a wide variety of changes in the last few years to become a flexible coating process for innovative surface functions. Today, barriers and multifunctional surfaces can meet complex requirements for a wide range of applications in a variety of sectors. New technological solutions for upgrading smart products as other emerging trends are developing.

Author Contributions: C.V. wrote the paper.

Funding: This research was funded by Romanian EEA Research Programme, MEN under the EEA Financial Mechanism 2009–2014, grant number No. 1SEE/2014 and the APC was funded by MDPI.

Conflicts of Interest: The author declares no conflict of interest.

References
1. Duncan, T.V. Applications of nanotechnology in food packaging and food safety: Barrier materials, antimicrobials and sensors. J. Colloid Interface Sci. 2011, 363, 1–24. [CrossRef] [PubMed]
2. Vasile, C. (Ed.) Polymeric Nanomaterials for Nanotherapeutics; Elsevier: Amsterdam, The Netherlands, 2019; ISBN 978-0-12-813932-5.
3. Grumazescu, A.M. (Ed.) Food Preservation, Nanotechnology in the Agri-Food Industry; Elsevier: Amsterdam, The Netherlands, 2017; Volume 5, ISBN Hardcover 9780128043035.
4. Chaudhry, Q. Nanotechnology Applications for Food Packaging. 2017. Available online: http://ilsi.eu/wp-content/uploads/sites/3/2016/06/S2.3-WSPM12-Chaudhry.pdf (accessed on 21 June 2017).
5. Huang, Q.; Given, P.; Qian, M. Micro/Nano-Encapsulation of Active Food Ingredients; American Chemical Society: Washington, DC, USA, 2009; Volume 1007, p. 314.
6. Irshad, A. Applications of Nanotechnology in Food Packaging and Food Safety (Barrier Materials, Antimicrobials and Sensors). 2013. Available online: http://www.slideshare.net/irshad2k6/applications-of-nanotechnology-in-food-packaging-and-food-safety-barrier-materials-antimicrobials-and-sensors (accessed on 14 June 2017).
7. Regulation (EC) No 1935/2004 of The European Parliament and of The Council of 27 October 2004 on Materials and Articles Intended to Come into Contact with Food and Repealing Directives 80/590/EEC and 89/109/EEC. Available online: https://www.interpack.com/cgi-bin/md_interpack/lib/pub/tt.cgi/Food_Safety.html?oid=55076&lang=2&ticket=g_u_e_s_t (accessed on 5 September 2018).

8. Aliofkhazraei, M. Nanocoatings: Size Effect in Nanostructured Films; Springer: Berlin, Germany, 2011; p. 212, ISBN 978-3-642-17966-2.

9. Brody, A.L. Nanocomposite technology in food packaging. *Food Technol.* 2007, 61, 80–83.

10. Brody, A.L.; Strupinsky, E.R.; Kline, L.R. *Active Packaging for Food Applications*; Technomic Pub. Co.: Lancaster, PA, USA, 2001; p. 218.

11. Kerry, J.; Butler, P. *Smart Packaging Technologies for Fast Moving Consumer Goods*; John Wiley: Chichester, UK; Hoboken, NJ, USA, 2008; p. 340.

12. De Azeredo, H.M.C. Nanocomposites for food packaging applications. *Food Res. Int.* 2009, 42, 1240–1253.

13. Polyethylene Plastic Packaging Applications—Packaging Blog. Available online: https://packagingblog.org/2014/02/08/polyethylene-plastic-packaging-applications/ (accessed on 5 September 2018).

14. Jin, T.; Zhang, H. Biodegradable Polylactic Acid Polymer with Nisin for Use in Antimicrobial Food Packaging. *J. Food Sci.* 2008, 73, 127–134. [CrossRef] [PubMed]

15. Mallegni, N.; Phuong, T.V.; Coltellli, M.-B.; Cinelli, P.; Laizzi, A. Poly(lactic acid) (PLA) Based Tear Resistant and Biodegradable Flexible Films by Blown Film Extrusion. *Materials* 2018, 11, 148. [CrossRef] [PubMed]

16. Xie, J.; Wang, Z.; Zhao, Q.; Yang, Y.; Xu, J.; Waterhouse, G.I.N.; Zhang, K.; Li, S.; Jin, P.; Jin, G. Scale-Up Fabrication of Biodegradable Poly(butylene adipate-co-terephthalate)/Organophilic–clay Nanocomposite Films for Potential Packaging Applications. *ACS Omega* 2018, 3, 1187–1196. [CrossRef]

17. ISO/TS27687:2008. This standard has been replaced by ISO/TS 80004-2:2015 ISO/TS 80004-2:2015(en) Nanotechnologies—Vocabulary—Part 2: Nano-objects: Nanotechnologies—Terminology and definitions for nano-objects—Nanoparticle, nanofibre and nanoplate.

18. Schadler, L.S.; Brinson, L.C.; Sawyer, W.G. Polymer Nanocomposites: A Small Part of the Story. Overview Nanocomposite Materials. *J. Mater.* 2007, 59, 53–60. [CrossRef]

19. Pedrazzoli, D. Understanding the Effect of Nanofillers on the Properties of Polypropylene and Glass Fiber/Polypropylene Multiscale Composites. Ph.D. Thesis, University of Trento, Trento, Italy, October 2014. Available online: http://eprints-phd.biblio.unitn.it/1322/1/Thesis_PhD_Pedrazzoli_2014.pdf (accessed on 13 June 2017).

20. Tiwari, J.N.; Tiwari, R.N.; Kim, K.S. Zero-dimensional, one-dimensional, two-dimensional and three-dimensional nanostructured materials for advanced electrochemical energy devices. *Prog. Mater. Sci.* 2012, 57, 724–803. [CrossRef]

21. LeBaron, P.C.; Wang, Z.; Pinnavaia, T.J. ˙. Polymer-layered silicate nanocomposites: An overview. *Appl. Clay Sci.* 1999, 15, 11–29. [CrossRef]

22. Pavlidou, S.; Papaspyrides, C.D. A review on polymer–layered silicate nanocomposites. *Prog. Polym. Sci.* 2008, 33, 1119–1198. [CrossRef]

23. Esposito Corcione, C.; Frigione, M. Characterization of Nanocomposites by Thermal Analysis. *Materials* 2012, 5, 2960–2980. [CrossRef]

24. Fernandez, A.; Torres-Giner, S.; Lagaron, J.M. Novel route to stabilization of bioactive antioxidants by encapsulation in electrospun fibres of zein prolamine. *Food Hydrocoll.* 2009, 23, 1427–1432. [CrossRef]

25. Reig, C.S.; Lopez, A.D.; Ramos, M.H.; Ballester, V.A.C. Nanomaterials: A Map for Their Selection in Food Packaging Applications. *Packag. Technol. Sci.* 2014, 27, 839–866. [CrossRef]

26. Sanchez-Garcia, M.D.; Lopez-Rubio, A.; Lagaron, J.M. Natural micro and nanobiocomposites with enhanced barrier properties and novel functionalities for food biopackaging applications. *Trends Food Sci. Technol.* 2010, 21, 528–536. [CrossRef]

27. Siracusa, V.; Rocculi, P.; Romani, S.; Rosa, M.D. Biodegradable polymers for food packaging: A review. *Trends Food Sci. Technol.* 2008, 19, 634–643. [CrossRef]

28. Smolander, M.; Chaudhry, Q. Nanotechnologies in Food Packaging. In *Nanotechnologies in Food*; Chaudhry, Q., Castle, L., Watkins, R., Eds.; RSC Publishing: London, UK, 2010; Chapter 6; pp. 86–101, ISBN 13: 978-0854041695, 10: 0854041699.
29. Lvov, Y.; Abdullayev, E. Functional polymer–clay nanotube composites with sustained release of chemical agents. *Prog. Polym. Sci.* 2013, 38, 1690–1719. [CrossRef]

30. Dufresne, A. Processing of Polymer Nanocomposites Reinforced with Polysaccharide Nanocrystals. *Molecules* 2010, 15, 4111–4128. [CrossRef] [PubMed]

31. Azizi Samir, M.A.S.; Alloin, F.; Sanchez, J.V.; Dufresne, A. Cross-linked nanocomposite polymer electrolytes reinforced with cellulose whiskers. *Macromolecules* 2004, 37, 4839–4844. [CrossRef]

32. Bhattacharya, M. Review Polymer Nanocomposites—A Comparison between Carbon Nanotubes, Graphene, and Clay as Nanofillers. *Materials* 2016, 9, 262. [CrossRef] [PubMed]

33. Kny, E. Polymer nanocomposite materials used for food packaging. In *Ecosustainable polymer NANOMATERIALS for Food Packaging. Innovative Solutions, Characterisation Needs, Safety and Environmental Issues*; Silvestre, C., Cimmino, S., Eds.; CRC Press Taylor & Francis Group: Boca Raton, FL, USA, 2013; Chapter 13; pp. 337–375, ISBN 9781138034266.

34. Liu, J.; Boo, W.-J.; Clearfield, A.; Sue, H.-J. Intercalation and Exfoliation: A Review on Morphology of Polymer Nanocomposites Reinforced by Inorganic Layer Structures. *Mater. Manuf. Process.* 2006, 21, 143–151. [CrossRef]

35. Oliveira, M.; Machado, A.V. Preparation of Polymer-Based Nanocomposites by Different Routes. 2013. Available online: https://repositorium.sdum.uminho.pt/bitstream/1822/26120/1/Chapter.pdf (accessed on 4 September 2018).

36. Bottom-up Methods for Making Nanotechnology Products. Available online: https://www.azonano.com/article.aspx?ArticleID=1079 (accessed on 4 September 2018).

37. Pal, S.L.; Jana, U.P.; Manna, K.; Mohanta, G.P.; Manava, R. Nanoparticle: An overview of preparation and characterization. *J. Appl. Pharma. Sci.* 2011, 01, 228–234.

38. Mittal, V. In-Situ Synthesis of Polymer Nanocomposites; Wiley-VCH: Hoboken, NJ, USA, Chapter 1; pp. 1–26. Available online: https://application.wiley-vch.de/books/sample/3527328793_c01.pdf (accessed on 6 September 2018).

39. Ahmad, M.B.; Gharayebi, Y.; Salit, M.S.; Hussein, M.Z.; Shameli, K. Comparison of In Situ Polymerization and Solution-Dispersion Techniques in the Preparation of Polyimide/Montmorillonite (MMT) Nanocomposite. *Int. J. Mol. Sci.* 2011, 12, 6040–6050. [CrossRef] [PubMed]

40. Darie, R.N.; Pâslaru, E.; Sdrobis, A.; Pricope, G.M.; Hitruță, A.; Baklavardis, A.; Vasile, C. Effect of Nanoclay Hydrophilicity on the Poly(lactic acid)/Clay Nanocomposites Properties. *Ind. Eng. Chem. Res.* 2014, 53, 7877–7890. [CrossRef]

41. Reddy, T.R.K.; Kim, H.-J.; Park, J.-W. Bio-nanocomposite Properties and its Food Packaging Applications. In *Ebook: Polymer Science: Research Advances, Practical Applications and Educational Aspects*; Méndez-Vilas, A., Solano, A., Eds.; Formatex Research Center: Badajoz, Spain, 2016; ISBN 978-84-942134-8-9. Available online: http://www.formatex.org/polymerscience1/ (accessed on 26 September 2018).

42. Lagaron, J.-M. (Ed.) *Multifunctional and Nanoreinforced Polymers for Food Packaging*; Woodhead Publishing Limited, Elsevier B.V.: Amsterdam, The Netherlands, 2011; pp. 485–497.

43. Mohanty, F.; Swain, S.K. Bionanocomposites for Food Packaging Applications. In *Nanotechnology Applications in Food. Flavor, Stability, Nutrition and Safety*; Oprea, A.E., Grumezescu, A.M., Eds.; Elsevier B.V.: Amsterdam, The Netherlands, 2018; Chapter 18; ISBN 978-0-12-811942-6363-379.

44. Wróblewska-Krepszutl, J.; Rydzkowski, T.; Borowski, G.; Szczypański, M.; Klepka, T.; Thakur, V.K. Recent progress in biodegradable polymers and nanocomposite-based packaging materials for sustainable environment. *Int. J. Polym. Anal. Charact.* 2018, 23, 383–395. [CrossRef]

45. Horst, M.F.; Quinzani, L.M.; Failla, M.D. Rheological and barrier properties of nanocomposites of HDPE and exfoliated montmorillonite. *Thermoplast. Compos. Mater.* 2014, 27, 106–125. [CrossRef]

46. Lagaron, J.M.; Sanchez-Garcia, M.; Gimenez, E. Thermoplastic nanobiocomposites for rigid and flexible food packaging applications. In *Environmentally Compatible Food Packaging*; Chellini, E., Ed.; Woodhead Publ. Ltd.: Cambridge, UK, 2008; Chapter 3; pp. 63–90, ISBN 9781845691943.

47. Petersson, L.; Oksman, K. Biopolymer based nanocomposites: Comparing layered silicates and microcrystalline cellulose as nanoreinforcement. *Compos. Sci. Technol.* 2006, 66, 2187–2196. [CrossRef]

48. Xu, Y.; Ren, X.; Hanna, M.A. Chitosan/clay nanocomposite film preparation and characterization. *J. Appl. Polym. Sci.* 2006, 99, 1684–1691. [CrossRef]
49. Marras, S.I.; Kladi, K.P.; Tsavintzelis, I.; Zuburtikudis, I.; Panayiotou, C. Biodegradable polymer nanocomposites: The role of nanoclays on the thermomechanical characteristics and the electrospun fibrous structure. *Acta Biomater.* 2008, 4, 756–765. [CrossRef] [PubMed]

50. Jang, W.S.; Rawson, I.; Grunlan, J.C. Layer-by-layer assembly of thin film oxygen barrier. *Thin Solid Films* 2008, 516, 4819–4825. [CrossRef]

51. Dean, K.; Yu, L.; Wu, D.Y. Preparation and characterization of melt extruded thermoplastic starch/clay nanocomposites. *Compos. Sci. Technol.* 2007, 67, 413–421. [CrossRef]

52. Yu, J.; Yang, J.; Liu, B.; Ma, X. Preparation and characterization of glycerol plasticized-PEA starch/ZnO-carboxymethylcellulose sodium nanocomposite. *Bioresour. Technol.* 2009, 100, 2832–2841. [CrossRef] [PubMed]

53. Fortunati, E.; Peltzer, M.; Armentano, I.; Torre, L.; Jiménez, A.; Kenny, J.M. Effects of modified cellulose nanocrystals on the barrier and migration properties of PLA nano-biocomposites. *Carbohydr. Polym.* 2012, 90, 948–956. [CrossRef] [PubMed]

54. Sung, S.H.; Chang, Y.; Han, J. Development of polylactic acid nanocomposite films reinforced with cellulose nanocrystals derived from coffee silversk. *Carbohydr. Polym.* 2017, 169, 495–503. [CrossRef] [PubMed]

55. Kvien, I.; Tanem, B.S.; Oksman, K. Characterization of cellulose whiskers and their nanocomposites by atomic force and electron microscopy. *Biomacromolecules* 2005, 6, 3160–3165. [CrossRef] [PubMed]

56. Chen, Y.; Liu, C.; Chang, P.R.; Cao, X.; Anderson, D.P. Bionanocomposites based on PEA starch and cellulose nanowhiskers hydrolyzed from pea hull fibre: Effect of hydrolysis time. *Carbohydr. Polym.* 2009, 76, 607–615. [CrossRef]

57. Svagan, A.J.; Hedenqvist, M.S.; Berglund, L. Reduced water vapour sorption in cellulose nanocomposites with starch matrix. *Compos. Sci. Technol.* 2009, 69, 500–506. [CrossRef]

58. Kvien, I.; Oksman, K. Orientation of cellulose nanowhiskers in polyvinyl alcohol. *Appl. Phys. A Mater. Sci. Process.* 2007, 87, 641–643. [CrossRef]

59. Martinez-Sanz, M.; Lopez-Rubio, A.; Lagaron, J.M. Cellulose nanowhiskers: Properties and applications as nanofiller in nanocomposites with interest in food packaging applications. In *Ecosustainable Polymer Nanomaterials for Food Packaging. Innovative Solutions, Characterisation Needs, Safety and Environmental Issues*; Silvestre, C., Cimmino, S., Eds.; CRC Press Taylor & Francis Group: Boca Raton, FL, USA, 2013; Chapter 8; pp. 195–219, ISBN 9781138034266.

60. Hellbert, W.; Cavaille, C.Y.; Dufresne, A. Thermoplastic nanocomposites filled with wheat straw cellulose whiskers. Part I: Processing and mechanical behaviour. *Polyom. Compos.* 1996, 17, 604–611. [CrossRef]

61. Chen, G.; Wei, M.; Chen, J.; Huang, J.; Dufresne, A.; Chang, P.R. Simultaneous reinforcing and toughening: New nanocomposites of waterborne polyurethane filled with low loading level of starch nanocrystals. *Polymer* 2008, 49, 1860–1870. [CrossRef]

62. Ljungberg, N.; Bonini, C.; Bortolussi, F.; Boisson, C.; Heux, L.; Cavaille, J.Y. New nanocomposite materials reinforced with cellulose whiskers in atactic polypropylene: Effect of surface and dispersion characteristics. *Biomacromolecules* 2005, 6, 2732–2739. [CrossRef] [PubMed]

63. Ljungberg, N.; Cavaille, J.Y.; Heux, L. Nanocomposites of isotactic polypropylene reinforced with rod-like cellulose whiskers. *Polymer* 2006, 47, 6285–6292. [CrossRef]

64. Lu, Y.; Weng, L.; Zhang, L. Morphology and properties of soy protein isolate thermoplastics reinforced with chinin whiskers. *Biomacromolecules* 2004, 5, 1046–1051. [CrossRef] [PubMed]

65. Sriupayo, J.; Supaphol, P.; Blackwell, J.; Rujiravanit, R. Preparation and characterization of a-chitin whisker-reinforced chitosan nanocomposite films with or without heat treatment. *Carbohydr. Polym.* 2005, 62, 130–136. [CrossRef]

66. De Moura, M.R.; Aouada, F.A.; Avena-Bustillos, R.J.; McHugh, T.H.; Krochta, J.M.; Mattoso, L.H.C. Improved barrier and mechanical properties of novel hydroxypropyl methylcellulose edible films with chitosan/tripolyphosphate nanoparticles. *J. Food Eng.* 2009, 92, 448–453. [CrossRef]

67. Ramanathan, T.; Abdala, A.A.; Stankovich, S.; Dikin, D.A.; Herrera-Alonso, M.; Piner, R.D.; Adamson, D.H.; Schniep, H.C.; Ruoff, R.S.; Nguyen, S.T.; et al. Functionalized graphene sheets for polymer nanocomposites. *Nat. Nanotechnol.* 2008, 3, 327–331. [CrossRef] [PubMed]

68. Moraru, C.I.; Panchapakesan, C.P.; Huang, Q.; Takhistov, P.; Liu, S.; Kokini, J.L. Nanotechnology: A new frontier in Food Science. *Food Technol.* 2003, 57, 24–29.

69. Brody, A.L. Nano and food packaging technologies converge. *Food Technol.* 2006, 60, 92–94.
70. Ling, S.; Chen, W.; Fan, Y.; Ke, Z.; Jin, K.; Haipeng, Y.; Buehler, M.J.; Kaplan, D.L. Biopolymer nanofibrils: Structure, modeling, preparation, and applications. Prog. Polym. Sci. 2018, 85, 1–56. [CrossRef]
71. Ling, S.; Kaplan, D.L.; Buehler, M.J. Nanofibrils in nature and materials engineering. Nat. Rev. Mater. 2018, 3, 1806. [CrossRef]
72. Xiong, R.; Grant, A.M.; Ma, R. Naturally-derived biopolymer nanocomposites: Interfacial design, properties and emerging applications. Mater. Sci. Eng. R Rep. 2018, 125, 1–41. [CrossRef]
73. You, J.; Zhu, L.; Wang, Z.; Zong, L.; Li, M.; Wu, X.; Li, C. Liquid Exfoliated Chitin Nanofibrils for Re-dispersibility and Hybridization of Two-Dimensional Nanomaterials. Chem. Eng. J. 2018, 44, 498–505. [CrossRef]
74. Barbash, V.A.; Yaschenko, O.V.; Shniruk, O.M. Preparation and Properties of Nanocellulose from Organosolv Straw Pulp. Nanoscale Res. Lett. 2017, 12, 241–249. [CrossRef] [PubMed]
75. Wulandari, W.T.; Rochliadi, A.; Arcana, I.M. Nanocellulose prepared by acid hydrolysis of isolated cellulose from sugarcane bagasse. IOP Conf. Ser. Mater. Sci. Eng. 2016, 107, 012045. [CrossRef]
76. Kargarzadeh, H.; Dufresne, A. Methods for Extraction of Nanocellulose from Various Sources; Wiley-VCH Verlag GmbH & Co. KGaA: Hoboken, NJ, USA, 2017; Available online: https://application.wiley-vch.de/books/sample/3527338667_c01.pdf (accessed on 25 September 2018).
77. Purdue University. Manufacturing Process Provides Low-Cost, Sustainable Option for Food Packaging. 2018. Available online: https://phys.org/news/2018-06-low-cost-sustainable-option-food-packaging.html#jCp (accessed on 25 September 2018).
78. Rahman, M.; Netravali, A.N. Oriented bacterial cellulose-soy protein based fully ‘green’ nanocomposites. Compos. Sci. Technol. 2016, 136, 85–93. [CrossRef]
79. Rahman, M.; Netravali, A.N. High-performance green nanocomposites using aligned bacterial cellulose and soy protein. Compos. Sci. Technol. 2017, 146, 183–190. [CrossRef]
80. Abdul Khalil, H.P.S.; Davoudpour, Y.; Liu, J.; Islam, M.N.; Mustapha, A.; Sude, K.; Dungani, R.; Jawaid, M. Production and modification of nanofibrillated cellulose using various mechanical processes: A review. Carbohydr. Polym. 2014, 99, 649–665. [CrossRef] [PubMed]
81. Martínez-Sanz, M.; Lopez-Rubio, A.; Lagarón, J.M. Optimization of the dispersion of unmodified bacterial cellulose nanowhiskers into polylactide via melt compounding to significantly enhance barrier and mechanical properties. Biomacromolecules 2012, 13, 3887–3899. [CrossRef] [PubMed]
82. Hoeng, F.; Denneulin, A.; Neuman, C.; Bras, J. Charge density modification of carboxylated cellulose nanocrystals for stable silver nanoparticles suspension preparation. J. Nanopart. Res. 2015, 17, 244. [CrossRef]
83. Trifol Guzman, J.; Szabo, P.; Daugaard, A.E.; Hassager, O. Hybrid Nanocellulose/Nanoclay Composites for Food Packaging Applications. Danmarks Tekniske Universitet, Kgs. Lyngby, Denmark, 2016. Available online: http://orbit.dtu.dk/files/128126567/Preprint_Jon_Trifol_Guzman.pdf (accessed on 4 September 2018).
84. Trifol, J.; Plackett, D.; Sillard, C.; Szabo, P.; Bras, J.; Daugaard, A.E. Hybrid poly(lactic acid)/nanocellulose/nanoclay composites with synergistically enhanced barrier properties and improved thermomechanical resistance. Polym. Int. 2016, 65, 988–995. [CrossRef]
85. Lopes, T.A.; Bufalino, L.; Cunha Claro, P.I.; Martins, M.A.; Tonoli, G.H.D.; Mendes, L.M. The effect of surface modifications with corona discharge in pinus and eucalyptus nanofibril films. Cellulose 2018, 25, 5017–5033. [CrossRef]
86. Singh, A.A.; Wei, J.; Vargas, N.H.; Geng, S.; Oksman, N.K. Synergistic effect of chitin nanocrystals and orientations induced by solid-state drawing on PLA-based nanocomposite tapes. Compos. Sci. Technol. 2018, 162, 140–145. [CrossRef]
87. Ling, S.; Qin, Z.; Li, C.; Huang, W.; Kaplan, D.L.; Buehler, M.J. Polymorphic Regenerated Silk Fibers Assembled Through Bioinspired Spinning. Available online: https://www.researchgate.net/publication/320959224_Polymorphic_regenerated_silk_fibers_assembled_through_bioinspired_spinning (accessed on 25 July 2018).
88. Araki, J.; Wada, M.; Kuga, S. Steric stabilization of a cellulose microcrystal suspension by poly(ethylene glycol) grafting. Langmuir 2001, 17, 21–27. [CrossRef]
89. Gopalan, N.K.; Dufresne, A.; Gandini, A.; Belgacem, M.N. Crab shells chitin whiskers reinforced natural rubber nanocomposites. 3. Effect of chemical modification of chitin whiskers. Biomacromolecules 2003, 4, 1835–1842. [CrossRef] [PubMed]
90. Angellier, H.; Molina-Boisseau, S.; Belgacem, M.N.; Dufresne, A. Surface chemical modification of waxy maize starch nanocrystals. Langmuir 2005, 21, 2425–2433. [CrossRef] [PubMed]

91. Nogi, M.; Abe, K.; Handa, K.; Nakatsuho, F.; Ifuku, S.; Yano, H. Property enhancement of optically transparent biomonofiber composites by acetylation. Appl. Phys. Lett. 2006, 89, 233123. [CrossRef]

92. Ifuku, S.; Nogi, M.; Abe, K.; Handa, K.; Nakatsuho, F.; Yano, H. Surface modification of bacterial cellulose nanofibers for property enhancement of optically transparent composites: Dependence on acetyl-group DS. Biomacromolecules 2007, 8, 1973–1978. [CrossRef] [PubMed]

93. Chen, Y.; Cao, X.; Chang, P.R.; Huneault, M.A. Comparative study on the films of poly(vinyl alcohol)/pea starch nanocrystals and poly(vinyl alcohol)/native pea starch. Carbohydr. Polym. 2008, 73, 8–17. [CrossRef]

94. Kristo, E.; Biliaderis, C.G. Physical properties of starch nanocrystal reinforced pullulan films. Carbohydr. Polym. 2007, 68, 146–158. [CrossRef]

95. Bin, Y.; Mine, M.; Koganemaru, A.; Jiang, X.; Matsuo, M. Morphology and mechanical and electrical properties of oriented PVA–VGCF and PVA–MWNT composites. Polymer 2006, 47, 1308–1317. [CrossRef]

96. Lopez Manchado, M.A.; Valentinii, L.; Biagotti, J.; Kenny, J.M. Thermal and mechanical properties of single-walled carbon nanotubes–polypropylene composites prepared by melt processing. Carbon 2005, 43, 1499–1505. [CrossRef]

97. Zeng, H.; Gao, C.; Wang, Y.; Watts, P.C.P.; Kong, H.; Cui, X.; Yan, D. In situ polymerization approach to multiwalled carbon nanotubes-reinforced nylon 10,10 composites: Mechanical properties and crystallization behavior. Polymer 2006, 47, 113–122. [CrossRef]

98. Wu, C.L.; Zhang, M.Q.; Rong, M.Z.; Friedrick, K. Tensile performance improvement of low nanoparticles filled-polypropylene composites. Compos. Sci. Technol. 2002, 62, 1327–1340. [CrossRef]

99. Vladimirov, V.; Betchev, C.; Vassiliou, A.; Papageorgiou, G.; Bikaris, D. Dynamic mechanical and morphological studies of isotactic polypropylene/fumed silica nanocomposites with enhanced gas barrier properties. Compos. Sci. Technol. 2006, 66, 2935–2944. [CrossRef]

100. Tang, S.; Zou, P.; Xiong, H.; Tang, H. Effect of nano-SiO2 on the performance of starch/polyvinyl alcohol blend films. Carbohydr. Polym. 2008, 72, 521–526. [CrossRef]

101. Xiong, H.G.; Tang, S.W.; Tang, H.L.; Zou, P. The structure and properties of a starch-based biodegradable film. Carbohydr. Polym. 2008, 71, 263–268. [CrossRef]

102. Makarem, M.; Pasbakhsh, P.; Cavallaro, G.; Lazzara, G.; Aw, Y.K.; Lee, S.M.; Milioto, S. Effect of Morphology and Size of Halloysite Nanotubes on Functional Pectin Bionanocomposites for Food Packaging Applications. ACS Appl. Mater. Interfaces 2017, 9, 17476–17488. [CrossRef] [PubMed]

103. Darie-Nită, R.N.; Vasile, C. Halloysite Containing Composites for Food Packaging Applications. In Composites Materials for Food Packaging; Cirillo, G., Kozlowski, M.A., Spizzirri, U.G., Eds.; Scrivener Publishing LLC: Beverly, MA, USA, 2018; Chapter 2; pp. 73–122, ISBN 978-1-119-16020-5.

104. Gaikwad, K.K.; Singh, S.; Lee, Y.S. High adsorption of ethylene by alkali-treated halloysite nanotubes for food-packaging applications. Environ. Chem. Lett. 2018, 16, 1055–1062. [CrossRef]

105. Tats, C.E.; Hendessi, S.; Baysal, M.; Unal, S.; Cebeci, F.C.; Menceloglu, Y.Z.; Unal, H. Halloysite Nanotubes/ Polyethylene Nanocomposites for Active Food Packaging Materials with Ethylene Scavenging and Gas Barrier Properties. Food Bioprocess Technol. 2017, 10, 789–798. [CrossRef]

106. Meister Meira, S.M.; Zehetmeyer, G.; Scheibel, J.M.; Orlandini Werner, J.; Brandelli, A. Starch-halloysite nanocomposites containing nisin: Characterization and inhibition of Listeria monocytogenes in soft cheese. LWT Food Sci. Technol 2016, 68, 226–234. [CrossRef]

107. Bugatti, V.; Viscusi, G.; Naddeo, C.; Gorrasi, G. Nanocomposites Based on PCL and Halloysite Nanotubes Filled with Lysozyme: Effect of Draw Ratio on the Physical Properties and Release Analysis. Nanomaterials 2017, 7, 213. [CrossRef] [PubMed]

108. Kim, H.; Abdala, A.A.; Macosko, C.W. Graphene/Polymer Nanocomposites. Macromolecules 2010, 43, 6515–6530. [CrossRef]

109. Allahbaksh, A. High barrier graphene/polymer nanocomposite films. In Food Packaging; Academic Press: Cambridge, UK, 2017; Chapter 20; pp. 699–737.

110. Dallasa, P.; Sharma, V.K.; Zborila, R. Silver polymeric nanocomposites as advanced antimicrobial agents: Classification, synthetic paths, applications, and perspectives. Adv. Colloid Interface Sci. 2011, 166, 119–135. [CrossRef] [PubMed]
111. Llorensa, A.; Lloret, E.; Picouet, P.A.; Trbojevich, R.; Fernandeza, A. Review. Metallic-based micro and nanocomposites in food contact materials and active food packaging. *Trends Food Sci. Technol.* **2012**, 24, 19–29. [CrossRef]

112. Yang, W.; Owczarek, J.S.S.; Fortunati, E.; Kozanecki, M.; Mazzaglia, A.; Balestra, G.M.M.; Kenny, J.M.M.; Torre, L.; Puglia, D. Antioxidant and antibacterial lignin nanoparticles in polyvinyl alcohol/chitosan films for active packaging. *Ind. Crops Prod.* **2016**, 94, 800–811. [CrossRef]

113. Dumitriu, R.P.; Stoica, I.; Vasilesescu, D.S.; Cazacu, G.; Vasile, C. Alginate/Lignosulfonate Blends with Photoprotective and Antioxidant Properties for Active Packaging Applications. *J. Polym. Environ.* **2018**, 26, 1100–1112. [CrossRef]

114. Sorrentino, A.; Gorrasi, G.; Vittoria, V. Review, Potential perspectives of bio-nanocomposites for food packaging applications. *Trends Food Sci. Technol.* **2007**, 18, 84–95. [CrossRef]

115. Kaci, M.; Benhamida, A.; Zaidi, L.; Touati, N.; Remili, C. Photodegradation of Polylactic acid/organ-modified clay nanocomposites under natural weathering exposure. In *Eco-sustainable Polymer Nanomaterials for Food Packaging. Innovative Solutions, Characterization Needs, Safety and Environmental Issues*; Silvestre, C., Cimmino, S., Eds.; CRC Press Taylor & Francis Group: Boca Raton, FL, USA, 2013; Chapter 11; pp. 281–315, ISBN 9781138034266.

116. Kozlowski, M.A.; Macyszyn, J. Recycling of nanocomposites. In *Eco-sustainable Polymer Nanomaterials for Food Packaging. Innovative Solutions, Characterization Needs, Safety and Environmental Issues*; Silvestre, C., Cimmino, S., Eds.; CRC Press Taylor & Francis Group: Boca Raton, FL, USA, 2013; Chapter 12; pp. 313–335, ISBN 9781138034266.

117. Bora, A.; Mishra, P. Characterization of casein and casein-silver conjugated nanoparticle containing multifunctional (pectin–sodium alginate/casein) bilayer film. *J. Food Sci. Technol.* **2016**, 53, 3704–3714. [CrossRef] [PubMed]

118. Tharanathan, R.N. Biodegradable films and composite coatings: Past, present and future. *Trends Food Sci. Technol.* **2003**, 14, 71–78. [CrossRef]

119. Arora, A.; Padua, G.W. Review: Nanocomposites in Food Packaging. *J. Food Sci.* **2010**, 75, R43–R49. [CrossRef] [PubMed]

120. Zhou, J.J.; Wang, S.Y.; Gunasekaran, S. Preparation and characterization of whey protein film incorporated with TiO$_2$ nanoparticles. *J. Food Sci.* **2009**, 74, N50–N56. [CrossRef] [PubMed]

121. Shi, L.; Zhou, J.; Gunasekaran, S. Low temperature fabrication of ZnO-whey protein isolate nanocomposite. *Mater. Lett.* **2008**, 62, 4383–4385. [CrossRef]

122. Chen, P.; Zhang, L. Interaction and properties of highly exfoliated soy protein/montmorillonite nanocomposites. *Biomacromolecules* **2006**, 7, 1700–1706. [CrossRef] [PubMed]

123. Yu, J.; Cui, G.; Wei, M.; Huang, J. Facile exfoliation of rectorite nanoplatelets in soy protein matrix and reinforced bionanocomposites thereof. *J. Appl. Polym. Sci.* **2007**, 104, 3367–3377. [CrossRef]

124. Liu, X.; Sun, W.; Wang, H.; Zhang, L.; Wang, J.Y. Microspheres of corn, zein, for an ivermectin drug delivery system. *Biomaterials* **2005**, 26, 109–115. [CrossRef] [PubMed]

125. Kijchavengkul, T.; Auras, R. Compostability of polymers. *Polym. Int.* **2008**, 57, 593–604. [CrossRef]

126. Zhao, R.; Torley, P.; Halley, P.J. Emerging biodegradable materials: Starch- and protein-based bio-nanocomposites. *J. Mater. Sci.* **2008**, 43, 3058–3071. [CrossRef]

127. Armentano, I.; Fuglia, D.; Luzi, F.; Arciola, C.R.; Morena, F.; Martino, S.; Torre, L. Nanocomposites Based on Biodegradable Polymers. *Materials* **2018**, 11, 795. [CrossRef] [PubMed]

128. Lu, D.R.; Xiao, C.M.; Xu, S.J. Starch-based completely biodegradable polymer materials. *Express Polym. Lett.* **2009**, 3, 366–375. [CrossRef]

129. Castro-Aguirre, E.; Auras, R.; Selke, S.; Rubino, M.; Marsh, T. Impact of Nanoclays on the Biodegradation of Poly(Lactic Acid) Nanocomposites. *Polymers* **2018**, 10, 202. [CrossRef]

130. Goodwin, D.D.; Boyer, I.; Devahif, T.; Gao, C.; Frank, B.P.; Lu, X.; Kuwama, L.; Gordon, T.B.; Wang, J.; Ranville, J.F.; et al. Biodegradation of Carbon Nanotube/Polymer Nanocomposites using a Monoculture. *Environ. Sci. Technol.* **2018**, 52, 40–51. [CrossRef] [PubMed]
132. Nanocoatings, Nanowerk. Available online: https://www.nanowerk.com/nanotechnology-news/newsid=47370.php (accessed on 4 September 2018).
133. Egodage, D.P.; Jayalath, H.T.S.; Samarasekara, A.M.P.B. Novel antimicrobial nano coated polypropylene based materials for food packaging systems. In Proceedings of the Moratuwa Engineering Research Conference (MERCon), Moratuwa, Sri Lanka, 29–31 May 2017.
134. Müller, K.; Bugnicourt, E.; Latorre, M.; Jordà, M.; Echegoyen Sanz, Y.; Lagaron, J.M.; Miesbauer, O.; Bianchin, A.; Hankin, S.; Bölz, U.; et al. Review on the Processing and Properties of Polymer Nanocomposites and Nanocoatings and Their Applications in the Packaging, Automotive and Solar Energy Fields. Nanomaterials 2017, 7, 74. [CrossRef] [PubMed]
135. Bastarrachea, L.J.; Wong, D.E.; Roman, M.J.; Lin, Z.; Goddard, J.M. Active Packaging Coatings. Coatings 2015, 5, 771–791. [CrossRef] [PubMed]
136. Vasile, C.; Pâslaru, E.; Sdrobis, A.; Pricope, G.; Ioanid, G.E.; Darie, R.N. Plasma assisted functionalization of synthetic and natural polymers to obtain new bioactive food packaging materials in Ionizing Radiation and Plasma discharge Mediating Covalent Linking of Stratified Composites Materials for Food Packaging. In Proceedings of the Co-Ordinated Project: Application of Radiation Technology in the Development of Advanced Packaging Materials for Food Products, Vienna, Austria, 22–26 April 2013; Safrany, A., Ed.; pp. 100–110. Available online: http://www-naweb.iaea.org/napc/iachem/working_materials/F2-22063-CR-1-report.pdf (accessed on 19 June 2017).
137. Cagri, A.; Ustunol, Z.; Ryser, E.T. Antimicrobial edible films and coatings. J. Food Prot. 2004, 67, 833–848. [CrossRef] [PubMed]
138. Smirnova, V.; Krasnoiarova, O.; Pridvorova, S.; Zherdev, A.; Gmoshinskii, I.; Kazydub, G.; Popov, K.; Khitichenko, S. Characterization of silver nanoparticles migration from package materials destined for contact with foods. Voprosy Pitaniia 2012, 81, 34–39. (In Russian) [PubMed]
139. Totolin, M. Plasma Chemistry and Natural Polymers; PIM Publisher: Iasi, Romania, 2007; pp. 15–25, ISBN 978-973-716-776-7.
140. Vasile, C.; Munteanu, B.S.; Zaharescu, T.; Ioanid, E.; Pamfil, D. Radiation Mediated Bioactive Compounds Immobilization on Polymers to Obtain Multifunctional Food Packaging Materials. In Proceedings of the International Conference on Applications of Radiation Science and Technology (ICARST’ 2017), Vienna, Austria, 23–28 April 2017.
141. Riccardi, C.; Zanini, S.; Tassetti, D. A Polymeric Film Coating Method on a Substrate by Depositing and Subsequently Polymerizing a Monomeric Composition by Plasma Treatment. Patent WO2014191901 A1, 4 December 2014.
142. Vasile, C. General survey of the properties of polyolefins. In Handbook of Polyolefins, 2nd ed.; Vasile, C., Ed.; Marcel Dekker: New York, NY, USA, 2000; pp. 401–416, ISBN 13: 978-0824786038, 10: 0824786033.
143. Bastarrachea, L.; Dhawan, S.; Sablani, S.S. Engineering properties of polymeric-based antimicrobial films for food packaging. Food Eng. Rev. 2011, 3, 79–93. [CrossRef]
144. Butnaru, E.; Stoleru, E.; Rapa, M.; Pricope, G.; Vasile, C. Development and manufacturing of formulations containing as active compounds CS and roseehip seeds oil by emulsion technique. In Proceedings of the 4th Technical Meeting of ActiBiosafe Project, Medias, Romania, 19–20 May 2016.
145. Caruso, R.A.; Antonietti, M. Sol–Gel Nanocoating: An Approach to the Preparation of Structured Materials. Chem Mater. 2001, 13, 3272–3282. [CrossRef]
146. Vasile, C.; Stoleru, E.; Irimia, A.; Zaharescu, T.; Dumitriu, R.P.; Ioanid, G.E.; Munteanu, B.S.; Oprica, L.; Pricope, G.M.; Hitruc, G.E. Ionizing Radiation and Plasma Discharge Mediating Covalent Linking of Bioactive Compounds onto Polymeric Substrate to Obtain Stratified Composites for Food Packaging. In Report of the 3rd RCM: Application of Radiation Technology in the Development of Advanced Packaging Materials for Food Products; Safrany, A., Ed.; IAEA: Vienna, Austria, 2016; Chapter 15; pp. 11–15.
147. Silvestre, C.; Cimmino, S.; Stoleru, E.; Vasile, C. Application of Radiation technology to food packaging. In Applications of Ionizing Radiation in Materials Processing; Sun, Y., Chmielewski, A., Eds.; Institute of Nuclear Chemistry and Technology: Warsaw, Poland, 2017; Chapter 20; pp. 461–485.
148. Goddard, J.M.; Hotchkiss, J.H. Polymer surface modification for the attachment of bioactive compounds. Prog. Polym. Sci. 2007, 32, 698–725. [CrossRef]
149. Moy, V.T.; Florin, E.L.; Gaub, H.E. Intermolecular forces and energies between ligands and receptors. Science 1994, 266, 257–259. [CrossRef] [PubMed]
150. Stoleru, E.; Zaharescu, T.; Hitruc, E.G.; Vesel, A.; Ioanid, E.G.; Coroaba, A.; Safrany, A.; Pricope, G.; Lungu, M.; Schick, C.; et al. Lactoferrin-immobilized surfaces onto functionalized PLA assisted by the gamma-rays and nitrogen plasma to create materials with multifunctional properties. *ACS Appl. Mater. Interfaces* 2016, 8, 31902–31915. [CrossRef] [PubMed]

151. Oniz-Magan, A.B.; Pastor-Blas, M.M.; Martin-Martinez, J.M. Different Performance of Ar, O₂ and CO₂ RF Plasmas in the Adhesion of Thermoplastic Rubber to Polyurethane Adhesive. In *Plasma Processes and Polymers*; D’Agostino, R., Favia, P., Oehr, C., Werheime, M.E., Eds.; Wiley-VCH: Weinheim, Germany, 2005; pp. 177–192.

152. Park, S.J.; Kim, J.S. Influence of Plasma Treatment on Microstructures and Acid–Base Surface Energetics of Nanostructured Carbon Blacks: N2 Plasma Environment. *J Colloid Interface Sci.* 2001, 244, 336–341. [CrossRef]

153. Bryjak, M.; Gancarcz, I.; Pozniak, G. Surface evaluation of plasma-modified polysulfone (Udel P-1700) films. *Langmuir* 1999, 15, 6400–6404. [CrossRef]

154. Strobel, M.; Lyons, C.S.; Mittal, K.L. *Plasma Surface Modification of Polymer: Relevance to Adhesion*; VSP: Utrecht, Germany, 1994; ISBN 90-6764-164-2.

155. Goddard, J.M.; Hotchkiss, J.H. Tailored functionalization of low-density polyethylene surfaces. *J. Appl. Polym. Sci.* 2008, 108, 2940–2949. [CrossRef]

156. Stoleru, E.; Dumitriu, R.P.; Munteanu, B.S.; Zaharescu, T.; Tanase, E.E.; Mitelut, A.; Ailiesei, G.-L.; Vasile, C. Novel Procedure to Enhance PLA Surface Properties By Chitosan Irreversible Immobilization. *Appl. Surf. Sci.* 2016, 367, 407–417. [CrossRef]

157. Stoleru, E.; Munteanu, S.B.; Dumitriu, R.P.; Coroaba, A.; Droboță, M.; Fras Zemljic, L.; Pricope, G.M.; Vasile, C. Polyethylene Materials with Multifunctional Surface Properties by Electrospaying Chitosan/Vitamin E Formulation Destined to Biomedical and Food Packaging Applications. *Iran. Polym. J.* 2016, 25, 295–307. [CrossRef]

158. Munteanu, B.S.; Dumitriu, R.P.; Profire, L.; Sacarescu, L.; Hitruc, G.E.; Stoleru, E.; Dobromir, M.; Matricala, A.L.; Vasile, C. Hybrid Nanostructures Containing Sulfadiazine Modified Chitosan as Antimicrobial Drug Carriers. *Nanomaterials* 2016, 6, 207. [CrossRef] [PubMed]

159. Pâslaru (Stoleru), E.; Munteanu, B.S.; Vasilie, C. Electrospun Nanostructures as Biodegradable Composite Materials for Biomedical Applications. In *Biodegradable Polymeric Nanocomposites Advances in Biomedical Applications*; Depan, D., Ed.; CRC Press, Taylor & Francis Group: Roca Baton, FL, USA, 2015; Chapter 3; pp. 49–73, ISBN 978-1-4666-0526-2.

160. Rabea, E.I.; Badawy, M.E.; Stevens, C.V.; Smagghe, G.; Steurbaut, W. Chitosan as antimicrobial agent: Applications and mode of action. *Biomacromolecules* 2003, 4, 1457–1465. [CrossRef] [PubMed]
168. Burton, G.W.; Traber, M.G. Vitamin E: Antioxidant activity, biokinetics, and bioavailability. *Annu. Rev. Nutr.* 1990, 10, 357–382. [CrossRef] [PubMed]

169. Vasile, C.; Sivertsvik, M.; Mitelut, A.C.; Brebu, M.A.; Stoleru, E.; Rosnes, J.T.; Tanase, E.E.; Khan, W.; Pamfil, D.; Cornea, C.; et al. Comparative Analysis of the Composition and Active Property Evaluation of Certain Essential Oils to Assess their Potential Applications in Active Food Packaging. *Materials* 2017, 10, 45. [CrossRef] [PubMed]

170. Kong, F.; Hu, Y.F. Biomolecule immobilization techniques for bioactive paper fabrication. *Anal. Bioanal. Chem.* 2012, 403, 7–13. [CrossRef] [PubMed]

171. Sdrobiš, A.; Biederman, H.; Kylian, O.; Vasile, C. Modification of cellulose/chitin mix fibers under different cold plasma conditions. *Cellulose* 2012, 20, 509–524. [CrossRef]

172. Barish, J.A.; Goddard, J.M. Topographical and chemical characterization of polymer surfaces modified by physical and chemical processes. *J. Appl. Polym. Sci.* 2011, 120, 2863–2871. [CrossRef]

173. Carlini, C.; Angiolini, L. Polymers as free radical photoinitiators. In *Synthesis and Photosynthesis*; Springer: Heidelberg, Germany, 1995; pp. 127–214. Available online: https://link.springer.com/bookseries/12 (accessed on 25 September 2018).

174. Hermanson, G.T. *Bioconjugate Techniques*, 3rd ed.; Academic Press: San Diego, CA, USA, 1996; 785p, ISBN 9780123822406. Hardcover ISBN 9780123822390.

175. Maeda, T.; Hagiwara, K.; Hasebe, T.; Hotta, A. Polymers with DLC Nanocoating by CVD Method for Biomedical Devices and Food Packaging in Comprehensive Guide for Nanocoatings Technology; Volume 3: Properties and Development; Nova Science Publishers: New York, NY, USA, 2015; pp. 405–433, ISBN 978-1-63482-647-1.

176. Technical Research Centre of Finland (VTT). Nanowerk News A Fully Recyclable Nanocoating for Food and Pharmaceuticals, 24 March 2010. Available online: http://www.nanowerk.com/news/newsid=15499.php (accessed on 23 June 2017).

177. SPALASTM SPALASTM (Spray Assisted Layer-by-Layer Assembly) Coating System. Available online: http://www.agiltron.com/PDFs/SPALASTM.pdf (accessed on 23 June 2017).

178. Bastarrachea, L.J.; McLandsborough, L.A.; Peleg, M.; Goddard, J.M. Antimicrobial N-Halamine modified polyethylene: Characterization, biocidal efficacy, regeneration, and stability. *J. Food Sci.* 2014, 79, E887–E897. [CrossRef] [PubMed]

179. Jokar, M.; Abdul Rahman, R. Study of silver ion migration from melt-blended and layered deposited silver polypylene nanocomposite into food simulants and apple juice. *Food Addit. Contam. Part A* 2014, 31, 734–742. [CrossRef] [PubMed]
188. Munteanu, B.S.; Aytac, Z.; Pricope, G.M.; Uyar, T.; Vasile, C. Polylactic acid (PLA)/Silver-NP/Vitamin E bionanocomposite electrospun nanofibers with antibacterial and antioxidant activity. J. Nanomater. Res. 2014, 16, 2643–2646. [CrossRef]

189. Vasile, C.; Darie-Niță, R.; Brebu, M.; Răpă, M.; Ștefan, M.; Stan, M.; Macavei, S.; Barbucu-Tudoran, L.; Borodi, G.; Vodnar, D.; et al. New PLA/ZnO/Cu/Ag bionanocomposites for food packaging. Express Polym. Lett. 2017, 11, 531–544. [CrossRef]

190. Munteanu, B.S.; Ioanid, G.E.; Pricope, G.M.; Mitelut, A.C.; Tanase, E.E.; Vasile, C. Development and manufacturing of capsules with active substances by electrospinning technique. Encapsulated forms. In Proceedings of the 4th Technical Meeting of ActiBiosafe Project, Medias, Romania, 19–20 May 2016.

191. Castro-Mayorga, J.L.; Fabra, M.J.; Cabedo, L.; Lagaron, J.M. On the Use of the Electrospinning Coating Technique to Produce Antimicrobial Polyhydroxyalkanoate Materials Containing In Situ-Stabilized Silver Nanoparticles. Nanomaterials 2017, 7, 4. [CrossRef] [PubMed]

192. Sanchez-Valdes, S.; Ortega-Ortiz, H.; Ramos-de Valle, L.F.; Medellin-Rodriguez, F.J.; Guedea-Miranda, R. Mechanical and antimicrobial properties of multilayer films with a polyethylene/silver nanocomposite layer. J. Appl. Polymer Sci. 2009, 111, 953–962. [CrossRef]

193. Garces, L.O.; de la Puerta, C.N. Antimicrobial Packaging Based on the Use of Natural Extracts and the Process to Obtain This Packaging. European Patent EP1657181-B1, 13 January 2010.

194. Lacroix, M. Use of Irradiation, for the Development of Active Edible Coatings, Beads and Packaging to Assure Food Safety and to Prolong Preservation. 2017. Available online: https://media.superevent.com/documents/20170425/1c03bea5d97576aa37769311cb3ae83b/m.-lacroix.pdf (accessed on 25 September 2018).

195. Min, M.; Shi, Y.; Ma, H.; Huang, H.; Shi, J.; Chen, X.; Liu, Y.; Wang, L. Polymer-nanoparticle composites composed of poly(3-hydroxybutyrate-co-3-hydroxyvalerate) and coated silver nanoparticles. J. Macromol. Sci. Part B 2015, 54, 411–423. [CrossRef]

196. Martinez-Abad, A.; Lagaron, J.M.; Ocizo, M.J. Characterization of transparent silver loaded poly(L-lactide) films produced by melt-compounding for the sustained release of antimicrobial silver ions in food applications. Food Control 2014, 43, 238–244. [CrossRef]

197. George, M.; Shen, W.-Z.; Qi, Z.; Bhatnagar, A.; Montemagno, C. Development and Property Evaluation of Poly (Lactic) Acid and Cellulose Nanocrystals Based Films with Either Silver or Peptide Antimicrobial Agents: Morphological, Permeability, Thermal, and Mechanical Characterization. IOSR J. Polym. Text. Eng. 2017, 4, 8–24. [CrossRef]

198. Girdthep, S.; Worajittiphon, P.; Leejarkpai, T.; Punyodom, W. Effect of Silver-loaded Kaolinite on Real Ageing, Hydrolytic Degradation, and Biodegradation of Composite Blown Films Based on Poly(lactic acid) and Poly(butylene adipate-co-terephthalate). Eur. Polym. J. 2016, 82, 244–259. [CrossRef]

199. Mbhele, Z.H.; Salemane, M.G.; van Sitter, C.G.C.E.; Nedeljkov, J.M.; Djokovic, V.; Luyt, A.S. Fabrication and characterization of silver-polyvinyl alcohol nanocomposites. Chem. Mater. 2003, 15, 5019–5024. [CrossRef]

200. Damm, C.; Munstedt, H.; Rosch, A. Long-term antimicrobial polyamide 6/silver-nanocomposites. J. Mater. Sci. 2007, 42, 6067–6073. [CrossRef]

201. Damm, C.; Munstedt, H.; Rosch, A. The antimicrobial efficacy of polyamide 6/silver-nano- and microcomposites. Mater. Chem. Phys. 2008, 108, 61–66. [CrossRef]

202. Cheng, Q.; Li, C.; Pavlinek, V.; Saha, P.; Wang, H. Surface-modified antibacterial TiO2/Ag+ nanoparticles: Preparation and properties. Appl. Surf. Sci. 2006, 252, 4154–4160. [CrossRef]

203. Li, H.; Li, F.; Wang, L.; Sheng, J.; Xin, Z.; Zhao, L.; Xiao, H.; Zheng, Y.; Hu, Q. Effect of nano-packing on preservation quality of Chinese jujube. Food Chem. 2009, 114, 547–552. [CrossRef]

204. Yu, H.; Sun, B.; Zhang, D.; Chen, G.; Yang, X.; Yao, J. Reinforcement of biodegradable poly(3-hydroxybutyrate-co-3-hydroxyvalerate) with cellulose nanocrystal/silver nanohybrids as bifunctional nanofillers. J. Mater. Chem. B 2014, 2, 8479–8489. [CrossRef]

205. Manso, S.; Becerril, R.; Nerin, C.; Gomez-Lus, R. Influence of pH and temperature variations on vapor phase action of an antifungal food packaging against five mould strains. Food Control 2015, 47, 20–26. [CrossRef]

206. Valderrama Solano, A.C.; Rojas de Gante, C. Two different processes to obtain antimicrobial packaging containing natural oils. Food Bioprocess Technol. 2012, 5, 2522–2528. [CrossRef]

207. Minelli, M.; de Angelis, M.G.; Doghieri, F.; Rocchetti, M.; Montenero, A. Barrier properties of organic-inorganic hybrid coatings based on polyvinyl alcohol with improved water resistance. Polym. Eng. Sci. 2010, 50, 144–153. [CrossRef]
208. Lantano, C.; Alfieri, I.; Cavazza, A.; Corradini, C.; Lorenzi, A.; Zuchetto, N.; Montenero, A. Natamycin based sol-gel antimicrobial coatings on polylactic acid films for food packaging. *Food Chem.* **2014**, *165*, 342–347. [CrossRef] [PubMed]

209. Jokar, M.; Alsing Pedersen, G.; Loeschner, K. Six open questions about the migration of engineered nano-objects from polymer-based food-contact materials: A review. *Food Addit. Contam. Part A* **2017**, *34*, 434–450. [CrossRef] [PubMed]

210. Zhu, Y.; Buonocore, G.G.; Lavorgna, M. Photocatalytic activity of PLA/TiO$_2$ nanocomposites and TiO$_2$-active multilayered hybrid coatings. *Ital. J. Food Sci.* **2012**, *24*, 102–106.

211. Makwana, S.; Choudhary, R.; Dogra, N.; Kohli, P.; Haddock, J. Nanoencapsulation and immobilization of cinnamaldehyde for developing antimicrobial food packaging material. *LWT Food Sci. Technol.* **2014**, *57*, 470–476. [CrossRef]

212. Theinsathid, P.; Visessanguan, W.; Kruenate, J.; Kingcha, Y.; Keeratipibul, S. Antimicrobial activity of lauric arginate-coated polylactic acid films against listeria monocytogenes and salmonella typhimurium on cooked sliced ham. *J. Food Sci.* **2012**, *77*, M142–M149. [CrossRef] [PubMed]

213. Guo, M.; Jin, T.Z.; Yang, R. Antimicrobial polylactic acid packaging films against listeria and salmonella in culture medium and on ready-to-eat meat. *Food Bioprocess Technol.* **2014**, *7*, 3293–3307. [CrossRef]

214. Auxier, J.A.; Schilke, K.F.; McGuire, J. Activity retention after nisin entrapment in a polyethylene oxide brush layer. *J. Food Prot.* **2014**, *77*, 1624–1629. [CrossRef] [PubMed]

215. Fernandes, S.C.M.; Sadocco, P.; Causio, J.; Silvestre, A.J.D.; Mondragon, I.; Freire, C.S.R. Antimicrobial pullulan derivative prepared by grafting with 3-aminopropyltrimethoxysilane: Characterization and ability to form transparent films. *Food Hydrocoll.* **2014**, *35*, 247–252. [CrossRef]

216. Muriel-Galet, V.; Talbert, J.N.; Hernandez-Munoz, P.; Gavara, R.; Goddard, J.M. Covalent immobilization of lysozyme on ethylene vinyl alcohol films for nonmigrating antimicrobial packaging applications. *J. Agric. Food Chem.* **2013**, *61*, 6720–6727. [CrossRef] [PubMed]

217. Anthierens, T.; Billiet, L.; Devlieghere, F.; du Prez, F. Poly(butylene adipate) functionalized with quaternary phosphonium groups as potential antimicrobial packaging material. *Innov. Food Sci. Emerg. Technol.* **2012**, *15*, 81–85. [CrossRef]

218. Mackiw, E.; Maka, L.; Sciezynska, H.; Pawlicka, M.; Dziadczyk, P.; Rzanek-Boroch, Z. The impact of plasma-modified films with sulfur dioxide, sodium oxide on food pathogenic microorganisms. *Packag. Technol. Sci.* **2015**, *28*, 285–292. [CrossRef]

219. Pinheiro, A.C.; Bourbon, A.I.; Medeiros, B.G.D.S.; da Silva, L.H.M.; da Silva, M.C.H.; Carneiro-da-Cunha, M.G.; Coimbra, M.A.; Vicente, A.A. Interactions between κ-carrageenan and chitosan in nanolayered coatings-structural and transport properties. *Carbohydr. Polym.* **2012**, *87*, 1081–1090. [CrossRef]

220. Carneiro-da-Cunha, M.G.; Cerqueira, M.A.; Souza, B.W.S.; Carvalhocz, S.; Quintas, M.A.C.; Teixeira, J.A.; Vicente, A.A. Physical and thermal properties of a chitosan/alginate nanolayered PET film. *Carbohydr. Polym.* **2010**, *82*, 153–159. [CrossRef]

221. Medeiros, B.G.D.S.; Pinheiro, A.C.; Teixeira, J.A.; Vicente, A.A.; Carneiro-da-Cunha, M.G. Polysaccharide/protein nanomultilayer coatings: Construction, characterization and evaluation of their effect on “Rocha” pear (*Pyrus communis* L.) shelf-life. *Food Bioprocess Technol.* **2012**, *5*, 2435–2445. [CrossRef]

222. Contini, C.; Álvarez, R.; O’Sullivan, M.; Dowling, D.P.; Gargan, S.O.; Monahan, F.J. Effect of an active packaging with citrus extract on lipid oxidation and sensory quality of cooked turkey meat. *Meat Sci.* **2014**, *96*, 1171–1176. [CrossRef] [PubMed]

223. Contini, C.; Katsikogianni, M.G.; O’Neill, F.T.; O’Sullivan, M.; Boland, F.; Dowling, D.P.; Monahan, F.J. Storage stability of an antioxidant active packaging coated with citrus extract following a plasma jet pretreatment. *Food Bioprocess Technol.* **2014**, *7*, 2228–2240. [CrossRef]

224. Bolumar, T.; Andersen, M.L.; Orlien, V. Antioxidant active packaging for chicken meat processed by high pressure treatment. *Food Chem.* **2011**, *129*, 1406–1412. [CrossRef]

225. Lee, C.H.; An, D.S.; Lee, S.C.; Park, H.J.; Lee, D.S. A coating for use as an antimicrobial and antioxidative packaging material incorporating nisin and α-tocopherol. *J. Food Eng.* **2004**, *62*, 323–329. [CrossRef]

226. Schreiber, S.B.; Bozell, J.J.; Hayes, D.G.; Zivanovic, S. Introduction of primary antioxidant activity to chitosan for application as a multifunctional food packaging material. *Food Hydrocoll.* **2013**, *33*, 207–214. [CrossRef]
227. Struller, C.F.; Kelly, P.J.; Copeland, N.J. Aluminum oxide barrier coatings on polymer films for food packaging applications. Surf. Coat. Technol. 2014, 241, 130–137. [CrossRef]

228. Chatham, H. Oxygen diffusion barrier properties of transparent oxide coatings on polymeric substrates. Surf. Coat. Technol. 1996, 78, 1–9. [CrossRef]

229. Shutava, T.G.; Prouty, M.D.; Agabekov, V.E.; Lvov, Y.M. Antioxidant properties of layer-by-layer films on the basis of tannic acid. Chem. Lett. 2006, 35, 1144–1145. [CrossRef]

230. Arrua, D.; Strumia, M.C.; Nazareno, M.A. Immobilization of Caffeic acid on a polypropylene film: Synthesis and antioxidant properties. J. Agric. Food Chem. 2010, 58, 9228–9234. [CrossRef] [PubMed]

231. Roman, M.J.; Tian, F.; Decker, E.A.; Goddard, J.M. Iron chelating polypropylene films: Manipulating photoinitiated graft polymerization to tailor chelating activity. J. Appl. Polym. Sci. 2014, 131, 39948. [CrossRef]

232. Ogiwara, Y.; Roman, M.J.; Decker, E.A.; Goddard, J.M. Iron chelating active packaging: Influence of competing ions and pH value on effectiveness of soluble and immobilized hydroxamate chelators. Food Chem. 2016, 196, 842–847. [CrossRef] [PubMed]

233. Tian, F.; Decker, E.A.; Clements, D.J.; Goddard, J.M. Influence of non-migratory metal-chelating active packaging film on food quality: Impact on physical and chemical stability of emulsions. Food Chem. 2014, 151, 257–265. [CrossRef] [PubMed]

234. Tian, F.; Decker, E.A.; Goddard, J.M. Controlling lipid oxidation via a biomimetic iron chelating active packaging material. J. Agric. Food Chem. 2013, 61, 12397–12404. [CrossRef] [PubMed]

235. Roman, M.J.; Decker, E.A.; Goddard, J.M. Performance of nonmigratory iron chelating active packaging materials in viscous model food systems. J. Food Sci. 2015, 80, 1965–1973. [CrossRef] [PubMed]

236. Tian, F.; Roman, M.J.; Decker, E.A.; Goddard, J.M. Biomimetic design of chelating interfaces. J. Appl. Polym. Sci. 2015, 132, 41231–41239. [CrossRef]

237. Wong, D.E.; Dai, M.; Talbert, J.N.; Nugen, S.R.; Goddard, J.M. Biocatalytic polymer nanofibers for stabilization and delivery of enzymes. J. Mol. Catal. B Enzym. 2014, 110, 16–22. [CrossRef]

238. Johansson, K.; Winestrand, S.; Johansson, C.; Järnstrom, L.; Jonsson, L.J. Oxygen-scavenging coatings and films based on lignosulfonates and laccase. J. Biotechnol. 2012, 161, 14–18. [CrossRef] [PubMed]

239. Mahoney, K.W.; Talbert, J.N.; Hotchkiss, J.H. Covalent attachment of lactase to low-density polyethylene films. J. Food Sci. 2007, 72, E36–E41. [CrossRef] [PubMed]

240. Mahoney, K.W.; Talbert, J.N.; Goddard, J.M. Effect of polyethylene glycol tether size and chemistry on the attachment of lactase to polyethylene films. J. Appl. Polym. Sci. 2013, 127, 1203–1210. [CrossRef]

241. Talbert, J.N.; Goddard, J.M. Influence of nanoparticle diameter on conjugated enzyme activity. Food Bioprod. Process. 2013, 91, 693–699. [CrossRef]

242. Wang, D.E.; Talbert, J.N.; Goddard, J.M. Layer by layer assembly of a biocatalytic packaging film: Lactase covalently bound to low-density polyethylene. J. Food Sci. 2013, 78, E853–E860. [CrossRef] [PubMed]

243. Ge, L.; Zhao, Y.; Mo, T.; Li, J.; Li, P. Immobilization of glucose oxidase in electrospun nanofibrous membranes for food preservation. Food Control 2012, 26, 188–193. [CrossRef]

244. Caseli, L.; Santos, D.S., Jr.; Foschini, M.; Goncalves, D.; Oliveira, O.N., Jr. Control of catalytic activity of glucose oxidase in layer-by-layer films of chitosan and glucose oxidase. Mater. Sci. Eng. C 2007, 27, 1108–1110. [CrossRef]

245. Winestrand, S.; Johansson, K.; Järnström, L.; Jönsson, L.J. Co-immobilization of oxalate oxidase and catalase in films for scavenging of oxygen or oxalic acid. Biochem. Eng. J. 2013, 72, 96–101. [CrossRef]

246. Shutava, T.G.; Kommireddy, D.S.; Lvov, Y.M. Layer-by-layer enzyme/polyelectrolyte films as a functional protective barrier in oxidizing media. J. Am. Chem. Soc. 2006, 128, 9926–9934. [CrossRef] [PubMed]

247. Soares, N.F.F.; Hotchkiss, J.H. Bitterness reduction in grapefruit juice through active packaging. Packag. Technol. Sci. 1998, 11, 9–18. [CrossRef]

248. Nunes, M.A.P.; Vila-Real, H.; Fernandes, P.C.B.; Ribeiro, M.H.L. Immobilization of naringinase in PVA-alginate matrix using an innovative technique. Appl. Biochem. Biotechnol. 2010, 160, 2129–2147. [CrossRef] [PubMed]

249. Krenkova, J.; Lacher, N.A.; Svec, F. Highly efficient enzyme reactors containing trypsin and endoproteinase LysC immobilized on porous polymer monolith coupled to MS suitable for analysis of antibodies. Anal. Chem. 2009, 81, 2004–2012. [CrossRef] [PubMed]
250. Yamada, K.; Iizawa, Y.; Yamada, J.; Hirata, M. Retention of activity of urease immobilized on grafted polymer films. J. Appl. Polym. Sci. 2006, 102, 4886–4896. [CrossRef]

251. Andersson, M.; Andersson, T.; Adlercreutz, P.; Nielsen, T.; Hornsten, E. Toward an enzyme-based oxygen scavenging laminate. Influence of industrial lamination conditions on the performance of glucose oxidase. Biotechnol. Bioeng. 2002, 79, 37–42. [CrossRef] [PubMed]

252. Park, H.P.; Braun, P.V. Coaxial Electrospinning of Self-Healing Coatings. Adv. Mater. 2010, 22, 496–499. [CrossRef] [PubMed]

253. Díez-Pascual, A.M. (Ed.) Antibacterial Activity of Nanomaterials; ISBN 978-3-03897-048-4 (Pbk); ISBN 978-3-03897-049-1 (PDF).

254. Wanga, J.; Huang, N.; Pan, C.J.; Kwok, S.C.H.; Yang, P.; Leng, Y.X.; Chen, J.Y.; Sun, H.; Wan, G.J.; Liu, Z.Y.; et al. Bacterial repellence from polystyrene terephthalate surface modified by acetylene plasma immersion ion implantation-deposition. Surf. Coat. Technol. 2004, 186, 299–305. [CrossRef]

255. Brobbey, K.J.; Saarinen, J.J.; Alakomi, H.-L.; Yang, B.; Toivakka, M. Efficacy Of Natural Plant Extracts In Antimicrobial Packaging Systems. J. Appl. Packag. Res. 2017, 9, 6.

256. Mitelü¸t, A.C.; Popa, E.E.; Popescu, P.A.; Popa, M.E.; Munteanu, B.S.; Vasile, C.; Ştefănoiu, G. Research on chitosan and oil coated PLA as food packaging material. Presented at the International Workshop, “Progress in Antimicrobial Materials”, Iasi, Romania, 30 March 2017.

257. Busolo, M.A.; Fernandez, P.; Ocio, M.J.; Lagaron, J.M. Novel silver-based nanoclay as an antimicrobial in polylactic acid food packaging coatings. Food Addit. Contam. Part A 2010, 27, 1617–1626. [CrossRef] [PubMed]

258. Luo, P.G.; Stutzenberger, F.J. Nanotechnology in the detection and control of microorganisms. In Advances in Applied Microbiology; Laskin, A.I., Sariaslani, S., Gadd, G.M., Eds.; Elsevier: London, UK, 2008; Volume 63, pp. 145–181, ISBN 9780120026623, 9780080468921.

259. Makwana, S.; Choudhary, R.; Kohli, P. Advances in Antimicrobial Food Packaging with Nanotechnology and Natural Antimicrobials. Int. J. Food Sci. Nutr. Eng. 2015, 5, 169–175. [CrossRef]

260. Li, Q.; Mahendra, S.; Lyon, D.Y.; Brunet, L.; Liga, M.V.; Li, D.; Alvarez, P.J.J. Antimicrobial nanomaterials for water disinfection and microbial control: Potential applications and implications. Water Res. 2008, 42, 4591–4602. [CrossRef] [PubMed]

261. Ghaffari-Moghaddam, M.; Eslahi, H. Synthesis, characterization and antibacterial properties of a novel nanocomposite based on polyaniline/polyvinyl alcohol/Ag. Arab. J. Chem. 2013, 7. [CrossRef]

262. Kumar, R.; Munstedt, H. Silver ion release from antimicrobial polyamide/silver composites. Biomaterials 2005, 26, 2081–2088. [CrossRef] [PubMed]

263. Hannon, J.C.; Cummins, E.; Kerry, J.; Cruz-Romero, M.; Morris, M. Advances and challenges for the use of engineered nanoparticles in food contact materials. Trends Food Sci. Technol. 2015, 43, 43–62. [CrossRef]

264. Drew, R.; Hagen, T.; ToxConsult Pty Ltd. Nanotechnologies in Food Packaging: An Exploratory Appraisal of Safety and Regulation, Report Prepared for Food Standards Australia New Zealand. May 2016. Available online: https://www.foodstandards.gov.au/publications/Documents/Nanotech%20in%20food%20packaging.pdf (accessed on 10 June 2017).

265. Qi, L.F.; Xu, Z.R.; Jiang, X.; Hu, C.; Zou, X. Preparation and antibacterial activity of chitosan nanoparticles. Carbohydr. Res. 2004, 339, 2693–2700. [CrossRef] [PubMed]

266. Kang, S.; Pinault, M.; Pfefferle, L.D.; Elimelech, M. Single-walled carbon nanotubes exhibit strong antimicrobial activity. Langmuir 2007, 23, 8670–8673. [CrossRef] [PubMed]

267. Tian, F.; Decker, E.A.; Goddard, J.M. Controlling lipid oxidation of food by active packaging technologies. Food Funct. 2013, 4, 669–680. [CrossRef] [PubMed]

268. Gomez-Estaca, J.; Lopez-de-Dicastillo, C.; Hernandez-Munoz, P.; Catala, R.; Gavara, R. Advances in antioxidant active food packaging. Trends Food Sci. Technol. 2014, 35, 42–51. [CrossRef]

269. Nerin, C.; Tover, L.; Salafranca, J. Behaviour of a new antioxidant active film versus oxidizable model compounds. J. Food Eng. 2008, 84, 313–320. [CrossRef]

270. Yemmireddy, V.K.; Farrell, G.D.; Hung, Y.C. Development of Titanium Dioxide (TiO2) Nanocoatings on Food Contact Surfaces and Method to Evaluate Their Durability and Photocatalytic Bactericidal Property. J. Food Sci. 2015, 80, N1903–N1911. [CrossRef] [PubMed]
271. Barbiroli, A.; Bonomi, F.; Capretti, G.; Iametti, S.; Manzoni, M.; Piergiovanni, L.; Rollini, M. Antimicrobial activity of lysozyme and lactoferrin incorporated in cellulose-based food packaging. *Food Control* **2012**, *26*, 387–392. [CrossRef]

272. Mendes de Souza, P.; Fernandez, A.; Lopez-Carballo, G.; Gavara, R.; Hernandez-Munoz, P. Modified sodium caseinate films as releasing carriers of lysozyme. *Food Hydrocoll.* **2010**, *24*, 300–306. [CrossRef]

273. Moskovitz, Y.; Srebnik, S. Mean-field model of immobilized enzymes embedded in a grafted polymer layer. *Biophys. J.* **2005**, *89*, 22–31. [CrossRef] [PubMed]

274. Robertson, G.L. *Food Packaging: Principles and Practice*, 2nd ed.; Taylor & Francis/CRC Press: Boca Raton, FL, USA, 2006; p. 550, ISBN 9781439862414.

275. Chan, C.M.; Ko, T.M.; Hiraoka, H. Polymer surface modification by plasmas and photons. *Surf. Sci. Rep.* **1996**, *24*, 3–54. [CrossRef]

276. Jansen, B.; Kohnen, W. Prevention of Biofilm Formation by Polymer Modification. *J. Ind. Microbiol.* **1995**, *15*, 391–396. [CrossRef] [PubMed]

277. Karkhanisa, S.S.; Stark, N.M.; Sabo, R.C.; Matuana, L.M. Water vapor and oxygen barrier properties of extrusion-blown poly(lactic acid)/cellulose nanocrystals nanocomposite films. *Compos. Part A Appl. Sci. Manuf.* **2018**, *114*, 204–211. [CrossRef]

278. López de Dicastillo, C.; Garrido, L.; Alvarado, N.; Romero, J.; Palma, J.L.; Galotto, M.J. Improvement of Polylactide Properties through Cellulose Nanocrystals Embedded in Poly(Vinyl Alcohol) Electrospun Nanofibers. *Nanomaterials* **2017**, *7*, 106. [CrossRef] [PubMed]

279. Chakrabarty, A.; Teramoto, Y. Review Recent Advances in Nanocellulose Composites with Polymers: A Guide for Choosing Partners and How to Incorporate Them. *Polymers* **2018**, *10*, 517. [CrossRef]

280. Ratner, B.D.; Hoffman, A.S. Physicochemical surface modification of materials used in medicine. In *Biomaterials Science: An Introduction to Materials in Medicine*, 3rd ed.; Ratner, B.D., Hoffman, A.S., Schoen, F.J., Lemons, J.E., Eds.; Academic Press: Oxford, UK; Waltham, MA, USA, 2013; pp. 259–276, ISBN 9780123746269, 9780080877808.

281. Wagner, J.R., Jr. *Multilayer Flexible Packaging Technology and Applications for the Food, Personal Care and Over-the-Counter Pharmaceutical Industries*, 1st ed.; Elsevier Science: Oxford, NY, USA, 2010; p. 258, ISBN 9780815520214, 9780815520221.

282. Nistor, M.T.; Vasile, C.; Chiriac, A.P.; Rusu, A.; Zgardan, C.; Nita, L.E.; Neamtu, I. Hybrid Sensitive Hydrogels for Medical Applications. In *Polymer Materials with Smart Properties*; Bercea, M., Ed.; Nova Science Publishers: New York, NY, USA, 2010; Volume 24, ISBN 978-1-60876-872-1.

283. Cheaburu, C.N.; Vasile, C. pH-responsive Hydrogels based on Chitosan and its derivatives. In *Material Science, Synthesis, Properties, Applications, Polyme Yearbook*; Pethrick, R.A., Zaikov, G.E., Eds.; Nova Science Publishers: New York, NY, USA, 2010; Volume 24, ISBN 978-1-60876-872-1.

284. Vasile, C.; Dumitriu, R.P. (Eds.) *Polymeric Materials Responsive to External Stimuli—Smart Polymeric Materials*; PIM Publishing House: Iasi, Romania, 2008; p. 285, ISBN 978-606-520-065-8.

285. Pamfil, D.; Vasile, C. Responsive Polymeric Nanotherapeutics. In *Polymeric Nanomaterials in Nanotherapeutics*; Vasile, C., Ed.; Elsevier: Amsterdam, The Netherlands, 2019; Chapter 2; p. 53.

286. Cordeiro, A.L. Stimuli-Responsive Polymer Nanocoatings, Nanotechnologies for the Life Sciences. In *Nanostructured Thin Films and Surfaces*; Challa, S.S., Kumar, R., Eds.; John Wiley and Sons: New York, NY, USA, 2011, Volume 5.

287. Nath, N.; Chilkoti, A. *Creating “Smart” Surfaces Using Stimuli Responsive Polymers*, Advanced Materials; WILEY-VCH Verlag GmbH & Co. KGaA: Weinheim, Germany, 2002.

288. Cohen Stuart, M.; Huck, W.; Genzer, J.; Müller, M.; Ober, C.; Stamm, M.; Sukhorukov, G.B.; Szleifer, I.; Tsukruk, V.V.; Urban, M.; et al. Emerging Applications of Stimuli-Responsive Polymer Materials. *Nat. Mater.* **2010**, *9*, 101–113. [CrossRef] [PubMed]

289. Wei, M.; Gao, Y.; Li, X.; Serpe, M.J. Stimuli-responsive polymers and their applications. *Polym. Chem.* **2017**, *8*, 10–11. [CrossRef]

290. Noonan, G.O.; Whelton, A.J.; Carlander, D.; Duncan, T.V. Measurement methods to evaluate engineered nanomaterial release from food contact materials. *Compr. Rev. Food Sci. Food Saf.* **2014**, *13*, 679–692. [CrossRef]
292. Honarvar, Z.; Hadian, Z.; Mashayekh, M. Nanocomposites in food packaging applications and their risk assessment for health. *Electron. Physician* 2016, 8, 2531–2538. [CrossRef] [PubMed]

293. Farhoodi, M. Nanocomposite Materials for Food Packaging Applications: Characterization and Safety Evaluation. *Food Eng. Rev.* 2016, 8, 35–51. [CrossRef]

294. Lan, T. Nanocomposite Materials for Packaging Applications, ANTEC. 2007. Available online: http://www.nanocor.com/tech_papers/ANTEC-2007.pdf (accessed on 25 September 2018).

295. BCC Research, The Advanced Packaging Solutions Market Value for 2017 Is Projected to Be Nearly $44.3 Billion. 2015. Available online: http://www.bccresearch.com (accessed on 20 June 2017).

296. Realini, C.E.; Marcos, B. Active and intelligent packaging systems for a modern society. *Meat Sci.* 2014, 98, 404–419. [CrossRef] [PubMed]

297. Day, B.P.F. Active packaging of foods. In *Smart Packaging Technologies for Fast Moving Consumer Goods*; Kerry, J.P., Butler, P., Eds.; Wiley & Sons, Ltd.: West Sussex, UK, 2008; pp. 1–18, ISBN 978-0-470-02802-5.

298. Barnes, K.A.; Sinclair, C.R.; Watson, D.H. Chemical Migration and Food Contact Materials, 1st ed.; Woodhead Publishing: Amsterdam, The Netherlands, 2007; p. 464, ISBN 9781845692094; Hardcover ISBN 9781845690298.

299. Farris, S.; Introzzi, L.; Piergiovanni, L.; Cozzolino, C.A. Effects of different sealing conditions on the seal strength of polypropylene films coated with a bio-based thin layer. *Ital. J. Food Sci.* 2011, 23, 111–114. [CrossRef]

300. Siegrist, M.M.-E.; Cousin, H.; Kastenholz, A.; Wiek, A. Public acceptance of nanotechnology foods and food packaging: The influence of affect and trust. *Appetite* 2007, 49, 459–466. [CrossRef] [PubMed]

301. Siegrist, M.; Stampfli, N.; Kastenholz, H.; Keller, C. Perceived Risks and Perceived Benefits of Different Nanotechnology Foods and Nanotechnology Food Packaging. *Appetite* 2008, 51, 283–290. [CrossRef] [PubMed]

302. Siegrist, M.; Sütterlin, B. Importance of perceived naturalness for acceptance of food additives and cultured meat. *Appetite* 2017, 113, 320–326. [CrossRef] [PubMed]

303. Bearth, A.; Siegrist, M. Are risk or benefit perceptions more important for public acceptance of innovative food technologies: A meta-analysis. *Trends Food Sci. Technol.* 2016, 49, 14–23. [CrossRef]

304. Marquis, D.M.; Guillaume, E.; Chivas-Joly, C. Properties of Nanofillers in Polymer. Chap 11. In *Nanocomposites and Polymers with Analytical Methods*; Cuppoletti, J., Ed.; IntechOpen: London, UK, 2011; Chapter 13; pp. 261–284. Available online: http://www.intechopen.com/books/nanocomposites-and-polymers-with-analytical-methods/properties-of-nanofillers-in-polymer (accessed on 25 September 2018).