

Review

# Natural Ingredients in Functional Coatings—Recent Advances and Future Challenges

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**Abstract:** In recent decades, coating materials have gained researchers’ interest, finding applications in different areas such as antimicrobial coatings for biomedical applications, coatings for increasing the shelf-life of commercial products, or coatings for the conservation of cultural heritage artifacts. The use of new types of coating materials based on natural ingredients can lead to the removal of harmful chemicals and contribute to the development of materials having different and promising properties. New challenges can appear both in the production process, as well as in the case of final application, when coating materials must be applied on various supports. The present review paper aims to be a critical discussion regarding the possibility of using natural ingredients as functional coatings, and to prove that the same material can be used in different fields, from the biomedical to environmental, or from cultural heritage protection to the food and cosmetic industries. The paper is based on the newest published studies, and its main goal is to be an inspiration source for researchers, in order to create more functional and applicable composite coatings in specific fields.

**Keywords:** functional coatings; natural materials; antimicrobial; food industry; environment protection; cultural heritage conservation



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## 1. Introduction

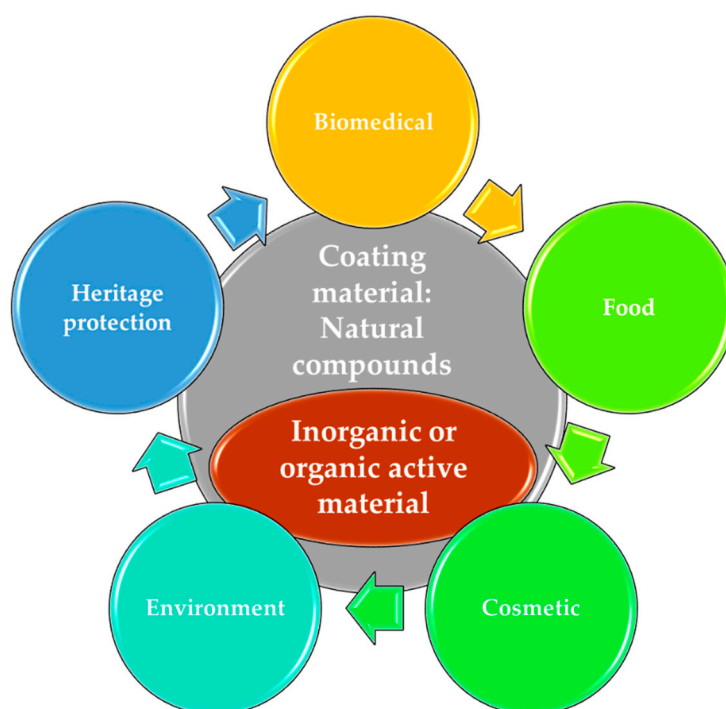
In recent decades, coating materials have gained researchers’ interest, and the registered progress has led to the evaluation of their potential use in different applications, including some of great importance, such as the development of antimicrobial coatings for biomedical applications, coatings applied for increasing the shelf-life of commercial products, or coatings used for the conservation of cultural heritage artifacts. In its widest sense, a coating represents a thin layer of material that, when deposited or applied on the surface of a support material, improves the surface properties of the substrates and creates a protective barrier against detrimental external factors [1]. Considering their envisaged properties and final applications, different types of coatings were developed, from monolayer to nanostructured and/or nanometric-scale multilayer coatings [2].

The permanent search for new types of coating materials, accompanied by the shift in consumer’s habits towards “bio-products” led to an increasing interest regarding the application of functional coatings based on natural products, especially in industries such as food or cosmetic. In the food industry, as an example regarding the potential of natural alternatives, the use of wax coatings on citrus (as a method to protect them against microbial spoilage) was known and applied in ancient China [3]; nowadays, the development of new materials and production technologies has new valences—to obtain enhanced biodegradability and eco-friendly properties [4].

For other applications, such as development of antifouling coatings, the interest is to replace classical used materials (such as tributyltin or zinc pyrithione), which can have negative effects on non-target organisms, with some natural-based alternatives [5].

Widely applied, natural and synthetic polymers are commonly used as coating layers, and their enrichment with nanoparticles, inorganic and organic materials increases the variety of available coatings, with the developed hybrid materials overcoming deficiencies by combining the advantages of each component [6,7].

The present review paper aims to represent a critical discussion regarding the possibility of applying natural ingredients (compounds obtained from natural sources) for the development of functional coatings, and to explore their possible applications in different areas which affects our daily life, from biomedical uses to environmental protection, or from cultural heritage conservation and restoration to food or cosmetic industries (Figure 1).



**Figure 1.** Schematic representation of the manuscript content.

The present work is based on the most recently published literature data, and its main goal is to be an inspiration source for researchers, in order to create more functional and applicable composite coatings in specific fields, based on natural ingredients.

## 2. Coating Materials for Biomedical Applications

Coating materials for biomedical applications are one of the most studied class of materials in the last decades. Various biomedical engineering applications emerged with the development of new materials: drug delivery systems, tissue engineering, or wound dressing composites. Various types of coatings, such as inorganic ceramics, polymers, or composite materials can be successfully applied for titanium or magnesium alloys, or 316 L stainless steel implants, possessing superior biocompatibility and biodegradation properties [8]. Surface modification via coating can remove implant-associated bacterial infections caused by bacteria such as *Staphylococcus aureus* or *Escherichia coli*; the materials used for implants undergo permanent improvements, including the search for new alternative coating materials, and, in the same time, development of methods for support material treatment, i.e., droplet elimination for the removal of any potential bacteria or dirt particles, thus offering a good adhesion and a proper behavior of the coating material [2].

Hydroxyapatite (HAP) is one of the most used inorganic materials in biomedical applications that has gained attention as a coating material on metallic implants, and not only due to its enhanced adhesion properties [9], but also for its biocompatibility and osteoconductivity [10]. The use of HAP is limited by the available deposition techniques, which can influence the properties of the material in relation with the support. Physical vapor deposition, dip coating, chemical vapor deposition, micro-arc oxidation, sol-gel, or thermal spraying are all suitable deposition methods, but for each of these methods, different aspects must be considered before the final decision regarding the deposition method selection is made: apparition of thermal effects (e.g., distortion, crack, phase changing, etc.), destructive effects of loose atmospheric protection (e.g., penetration of inclusions and contaminations into the substrate) and, of particular importance, the properties of the coating materials [11].

The most important parameter in the selection of the coating method is represented by the biomaterial's envisaged application [12]. For example, among the disadvantages of dip coating, of particular importance is the low mechanical properties such as adhesion strength when compared to plasma spray coating, which is cost effective and protects the metal surface from corrosion [13]. Through plasma electrolytic oxidation (PAE), there can be obtained better mechanical properties than those produced by anodic oxidation and superior adhesion strengths, compared with plasma spraying [14]. Moreover, the morphology and the stability of HAP can limit its utilization in biomedical applications. The drawbacks of deposition techniques based on high temperature are related to the thermal behavior of HAP, which can lead to the degradation of the coating material [15]; this drawback can be overcome by the alteration of the classical HAP structure, usually by the substitution of calcium with other metals [16,17]. Moreover, modifying the HAP classical structure, the materials can achieve enhanced antimicrobial properties. As the field of materials for biomedical applications is shifted towards the use of modified scaffolds, in this area materials can be obtained with the mechanical advantages of the bio-ceramic materials properties [18,19]. Besides the previous presented advantages of modification of the classical structure of HAP used for medical implants, a disadvantage can be the long-term cytotoxicity, thus infecting red blood cells, a negative aspect that can be removed by producing composite coatings with a combination of polymer and ceramic materials [20]. Instead of using a structurally modified HAP for its antimicrobial properties, the possible cytotoxicity of the classical material can be removed by using natural products, especially secondary metabolites from plants [21].

For bone implants, an application for which metallic alloys are usually used due to the lack of adsorption sites, a challenge in the deposition of coating materials such as hydroxyapatite (in its classical or modified structure) without any special technique, is the use of different chelating agents or adhesive materials, with no alteration of the coating properties [22–24].

As potential coating material for biomedical applications, hydroxyapatite from natural sources with improved mechanical properties was studied by different authors. Utomo et al. studied hydroxyapatite synthesis, from the calcite rock from Jember, Indonesia, increasing its Vickers hardness up to 78.50 HVN, by adding polyethylene glycol [25]. A larger amount of magnesium in the coating materials was proven to stimulate an activity of new bone tissue in the study of Bootchanont et al. regarding the development of coatings based on HAP synthesized from fish bones [26]. By re-sintering pigeon bones wastes at 850, 950, 1050, and 1150 °C, a natural HAP was obtained with particle sizes in the range of 50–250 nm and a Ca/P ratio of 1.7, the compressive strength enhanced from 23.18 to 47.57 MPa, and with enhanced activity and proliferation of osteoblast cells in comparison with synthetic HAP [27]. Some recent advancements in the area of natural coatings applied in the biomedical area are presented in Table 1.

**Table 1.** Recent advances regarding coating materials for implants.

Coating Material	Medical Application	Method of Obtaining Coating Material/Deposition Technique	Properties of the Material	Ref.
Nano-HAP/Graphene oxide	Coating for bone implants	Precipitation method/-	HAP—Rod shaped morphology; Graphene oxide—plates	[28]
Ag(I) doped HAP	Coating on dentine	Precipitation method/-	-	[29]
Ag doped HAP/PLA composite	Bone coating material	Fused deposition technique-/Dip coating	Elongated rod-shaped morphology, 50 nm	[30]
Mg-HAP	Coating for Ti <sub>6</sub> Al <sub>4</sub> V alloy—dental application	-/Plasma electrolytic oxidation	Pore size—99.30–28.55 μm	[31]
Fe <sub>3</sub> O <sub>4</sub> doped HA/chitosan	Biomedical implants	Co-precipitation technique/electrophoretic deposition	Thickness of coatings—10 ± 0.2 μm	[32]
Cu-HAP/functionalized multiwall carbon nanotube	Coating for 316L stainless steel	Precipitation method/spray pyrolysis	Crystallite size—22 nm	[33]
Calcium silicate reinforced HAP	Ti <sub>6</sub> Al <sub>4</sub> V medical implant	-/atmospheric plasma spray	Spherical particles—1–10 μm	[34]
Hydroxyapatite and TiO <sub>2</sub> suspension	Nickel-free austenitic stainless steel	-/Electrophoretic coating process	Coating thickness—71.2–104.1 μm	[35]
Bio-glass reinforced with HAP	TiO <sub>2</sub> nanotubes	Chemical method/electrophoretic deposition	Coating thickness of 10–12 μm	[36]
Lithium-doped HAP	Biomedical applications	Pulsed laser deposition process	Diameter 25–50 nm	[37]

Hydroxyapatite's properties and applicability can be enhanced by developing different composite materials, in order to achieve superior behavior in biomedical applications. Nano-hydroxyapatite/graphene oxide, as a potential composite material for medical implant coating applications, gained Kaviya and coworkers' attention due to graphene oxide chemical and mechanical stability, magnetic behavior, thermal and electrical conductivity [28]. The synthesis of the composite material, using water as a mixture media, presented better morphological characteristics for the targeted application than those obtained in alcoholic media (flaky texture reflecting its layered microstructure), thus proposing water as a proper solvent, instead of toxic organic solvents. Silver ions proved to enhance nano-sized hydroxyapatite (nHAp) properties. Synthesized by the precipitation method, HAP-Ag composite can be used as a coating material, with superior properties compared with HAP, for the remineralization of dentine samples, contributing to the viability of L929 fibroblast cells (percentage cell viability for HAP-Ag—139.04, for HAP—137.85) and providing an antibacterial effect against bacteria such as *Streptococcus mutans*, *Candida albicans*, and *Escherichia coli*, in a reduced time of action [29]. By modifying the HAP-Ag scaffold with polyvinyl alcohol, Lett et al. obtained an enhanced material with better antimicrobial properties and 0.8% hemolytic activity, less than pure HAP (2%), which recommends it as a proper candidate, compatible with human blood [30]. PLA scaffolds influence the crystallinity and porosity of HAP-Ag, offering more protein adsorption, which is beneficial for an implant material, and, moreover, a bending strength (125 MPa) comparable to the strength of cortical bone.

Changing the P/Ca ratio from the synthesis process by adding other metallic ions than silver or metallic oxides, the morphology of HAP can be tailored; thus, the bioactive properties can be enhanced by releasing active ions in the media [31–33].

Other materials, which are usually used for enhancing mechanical properties, can be used to protect HAP degradation in thermal depositing processes and increase its healing properties. Singh et al. used calcium silicate to improve microhardness (238 HV for calcium silicate—HAP, respectively 194 HV for HAP) and porosity of pure HAP (19% calcium silicate—HAP, respectively 16% for HAP), a higher porosity conducting to improvement in the bond strength, avoiding interfacial failure and reducing the healing time and a high success rates of implantation [34]. Moreover, addition of calcium silicate improves the coating crystallinity, which indicates that the amount of the secondary phases such as  $\alpha$ -tricalcium phosphate,  $\beta$ -tricalcium phosphate, tetracalcium phosphate, and calcium oxide decreased in the coating material by thermal degradation. Tangestani and Hadianfard used polycaprolactone as a binder for production of the electrolyte suspensions in the

electrophoretic process of applying a HAP-TiO<sub>2</sub> composite to nickel-free austenitic stainless steel, improving the adhesion strength and creating a smoother surface with minimal or no cracks or pores at a certain amount of binder (2 g/L), because increasing the polymer concentration leads to an increase in viscosity and a decrease in zeta potential [35]. As another modality to enhance the adhesion of HAP as coating material on titanium substrate, Khanmohammadi et al. presented titania nanotube (TNT) arrays as an intermediate layer between ceramic coating and base surface, thus boosting the antibacterial effect [36].

Other compounds from the class of ceramics used as coating materials with enhanced properties were highlighted in different studies. Poly-L-lactic acid-akermanite-doxycycline coating on Ca-Mg-Zn alloy increased MG-63 cell attachment [38], hardystonite increased the attachment and spread of MC3T3-E1 osteoblastic cells [39], strontium-hardystonite-gahnite, a potential coating material for implants, revealed higher results of microhardness, nano-hardness and elastic moduli than those shown for the HAP coating [40], while diopside-coated AZ91 Mg alloy provided suitable protein adsorption sites [41].

Another important biomedical application of coatings is represented by the development of new wound healing dressings. Coatings with applications in tissue engineering and regenerative medicine must possess enhanced physicochemical and mechanical properties, biocompatibility, biodegradability and a bio-mimicking ability at the anatomical site. Instead of traditional materials (i.e., gauze), the advantages of modern wound healing dressing are tremendous: fast recovery caused by proliferation of unaffected cells, preservation of proper moisturizing, diffusion of active molecules, that can occur freely in any direction, an easier air penetration, all accompanied by the transparency of the material which offers the possibility to control the healing process without unnecessarily exposing the wound [42].

Choosing a proper coating material in which an active substance can be incorporated conduct to a successful wound management, thus facilitating and accelerating the healing process (Figure 2). An ideal material must be safe, non-irritant, easy to apply, pain-free, cost-effective and highly absorbent [43].



Figure 2. Schematic representation of a wound management process.

Most often, wound healing dressings are used in hemostatic strategy, so the main properties of the material are to rapidly absorb blood and to concentrate red blood cells, in order to achieve an efficient hemostasis [44]. When active substances (synthetic pharmaceuticals or natural compounds) cannot be used alone, composite materials based on different polymers can be developed for enhancing their properties. Due to their effective biocompatibility and biodegradability, natural polymers used for coatings in medical devices, such as chitosan, starch, alginate, collagen, gelatin, or silk, were reported by different authors [45–47]. Moreover, different studies revealed that the construction of such medical devices in the form of a layer-by-layer coating can generate multi-component coatings with an increased ability to regulate the release of active substances [48–50]. Additionally, these devices are used to create a physical barrier against exterior infections, by covering the wound surface and ensuring the diffusion of various nutrients and metabolites exchange between cells and scaffolds [51].

A promising approach to wound treatment is represented by the development of a composite material which could combine all desirable properties, the coating and the active substances contributing synergistically to the wound healing process. In some cases, coating materials are based on a single component, however the most encountered are the multiple-components coatings (Table 2). These coating materials can be in form of hydrogels, films or delivery systems deposited on support materials, their main characteristic being a good compatibility between the components and the active substances [52]. For the development of a proper coating material, various aspects need to be considered: (i) when the coating is obtained only from polymers (natural or synthetic), the advantage is the flexibility of the material, but the drawback is the lack of mechanical strength and chemical stability [53]; (ii) for coatings obtained only from inorganic materials, there is a poor adhesive strength on surfaces, film-forming ability, or the tendency to aggregate [54]; (iii) lack of stability and reduced activity under infection conditions and variable pH of different active substances can be removed by the proper use of the coating material [55]; (iv) the additives used to enhance the beneficial properties must not affect the main properties and the functionality of the primary coating material (i.e., antimicrobial) [56].

For single component coating materials, Aubert-Viard et al. controlled the cationic charge density of an antibacterial textile by the reaction time and the concentration of the reagents, and further coated it by a first layer consisting of a natural polymer (chitosan), immobilized by crosslinking with genipin, a polycarboxylic acid, and by thermal treatment, thus influencing the cytocompatibility and degradation of the material [57]. Blending inorganic compounds into a polymer coating can lead to the enhancement of the tensile strength between the layers, omitting the crosslinking process between them, without blocking their pores [58]. The polymer coating modification can be performed through chemical, radiation, or enzymatic methods [59,60]. Multiple-layer coatings have the advantage of the properties specific to each layer, thus accelerating the wound healing process [61]. Additionally, the lipopeptide incorporated membranes are potential candidates in wound healing dressing, due to their hemocompatibility along with a pH similar to the skin and the antibacterial properties, conferred by their electrostatic interaction onto the bacterial membrane with the subsequent disruption of cell membrane [62].

**Table 2.** Coating materials based on single and multiple support materials.

Coating Material	Active Substances	Properties	Ref.
Single components			
Chitosan	Chlorhexidine	Antibacterial activity against <i>Staphylococcus aureus</i>	[57]
Polyvinyl alcohol	Lipopeptides and zinc oxide nanoparticles	Antibacterial against <i>S. aureus</i> , <i>Klebsiella pneumoniae</i> and <i>Pseudomonas aeruginosa</i>	[62]
Alginate	Amniotic fluid	Superior cellular proliferation and enhanced collagen secretion	[63]
Two components			
Chitin/poly (lactic-coglycolic acid)	Fibroblast growth factor 2-hyaluronic acid	Antibacterial against <i>S. aureus</i> and <i>Escherichia coli</i>	[64]
Cellulose/chitosan	Self-antimicrobial	Antibacterial against <i>S. aureus</i> and <i>E. coli</i>	[58]
Alginate/gum acacia	Ampicillin and norfloxacin	Antibacterial against gram-positive and gram-negative bacteria	[65]
Chitosan/collagen	Arginine, alanine and phenylalanine	Pro-angiogenic ability	[66]
Chitosan/l-glutamic acid	Ag nanoparticles	Antibacterial against <i>E. coli</i> and <i>S. aureus</i>	[67]
Polyvinyl alcohol/chitosan	Chlorhexidine and polyhexanide	Antibacterial against <i>S. aureus</i> and <i>S. epidermidis</i>	[68]
Alginate/carboxymethyl chitosan	Kangfuxin	Accelerate blood coagulation	[69]
Chitosan/alginate	Gentamicin	Antibacterial against <i>E. coli</i> and <i>S. aureus</i>	[70]
Multiple components			
Chitosan/poly- $\gamma$ -glutamic acid/pluronic	Curcumin	Neocollagen regeneration and tissue reconstruction	[71]
Gelatine/poly-dopamine/chitosan	Carbon nanotubes	Antibacterial against <i>E. coli</i> and <i>S. aureus</i>	[72]
Polyvinyl alcohol/sodium alginate/chitosan	Ag nanoparticles loaded chitosan	Antibacterial against <i>E. coli</i> and <i>S. aureus</i>	[61]
Gelatin/sodium alginate/hyaluronic acid/reduced graphene oxide	Ibuprofen	Anti-inflammatory	[73]
Alginate/gelatin/carboxymethyl cellulose	Ag nanoparticles	Antibacterial against <i>E. coli</i> and <i>S. aureus</i>	[74]

Composite coatings can combine the advantages of multiple components, overcoming the drawbacks of the single components, transforming the biomedical devices into better tools, in order to satisfy the clinical requirements. Different dual systems are presented in the literature, each of them having their own advantages [64–70]. Chitin/poly (lactic-coglycolic acid) coating system can facilitate wound healing within 15 days in basic medium, achieving a FGF2 (fibroblast growth factor) able to promote the proliferation and migration of fibroblasts, being also a broad-spectrum antibacterial material with activity against drug-resistant bacteria [64]. Alginate/gum acacia represents a cheap coating material for synthetic drugs, presenting a rapid and high absorption capability in the range of 1022–2419% at pH 5.5 simulating wound exudates, and 2268–5042% at a pH 7.4 simulating blood within a period of 1–3 h [65]. In addition to chitosan/collagen-based hydrogels, amino acids (such as arginine, alanine and phenylalanine) are a source of building proteins, support endothelial cells proliferation and trigger angiogenesis [66]. The spongy composite

chitosan-l-glutamic acid, due to its structure, can immobilize metallic nanoparticles with antimicrobial properties and release them to the damaged area [67]. Additionally, a cheap solution is offered by the polyvinyl alcohol/chitosan system, but it can be used especially on wounds with low level of exudate production, being hydrophilic and presenting high swelling and water retention capacity [68]. Properties such as suitable water vapor transmittance, cytocompatibility, rapid hemostasis and elastic properties are present for alginate/carboxymethyl chitosan coatings and transform them into better wound healing dressing than commercial products [69].

Multiple components coatings can offer more advantages than the ones described above; more components into the matrix can offer superior properties to the final material [61,71–74].

A special interest gained the use of natural ingredients for different wound therapies, especially in order to prevent the development of bacterial resistance to antibiotics, natural compounds being a viable alternative treatment for multidrug resilient microorganisms [75]. Coatings containing nanoparticles synthesized by chemical routes were developed for traditional cotton fabrics and deposited on the surface via numerous techniques, such as the sol-gel method, sonochemical method, or pad dry cure method [76]. Phytosynthesized nanoparticles (nanoparticles obtained using natural extracts, for which the phytocomponents acts as both reducing and capping agents) proved to be more effective as antibacterial agents, being an alternative to the chemical compounds, providing long term durability against the microbial growth in an exterior of traditional cotton fabrics, by harnessing the antimicrobial properties of the nanoparticles and of the phytocomponents involved [77]. Moreover, plants extracts can be loaded into various polymers, enhancing hemostasis and speeding up tissue regeneration [78,79], or coated on the polymer support, thus being a simple, reproducible and cost-effective approach [80]. For wound healing dressings in the form of hydrogels, natural extracts can modify the morphology of the bio-composite by suppressing the crystallinity behavior [81] an important aspect being represented by the condition for the pores of the support material to have proper dimensions, to achieve the release of the encapsulated drugs and molecules, as well as to prevent the bacterial invasion [82].

### 3. Coating Materials for Different Industries

#### 3.1. Food Industry

Recently, different materials were developed, in order to be used in the food industry to prolong the shelf-life of food products, presented as packings or even coatings used as layers on commercialized merchandise. The interest in using natural compounds started in controlling the postharvest disease of fruits and vegetables [83]. Usually, these coatings are based on natural materials, classified, according to their origin, as of animal origin (casein, gelatin, collagen, etc.), and of vegetable origin (proteins, polysaccharides, waxes, etc.) [84]. In contrast to the harmful chemicals, natural functional coatings represent a non-toxic, biocompatible and biodegradable alternative. This type of coatings can decrease the respiration level and migration of water for perishable products [85], and, serve as good delivery vectors for antimicrobial substances, nutraceuticals and flavors [86].

For obtaining coatings as edible films for the food industry, the methods are based on two different routes, wet and dry processes, each of them having advantages and drawbacks, related not only to the raw materials, but also the envisaged application. They are based on solvent casting and extrusion processes, solubility of the materials being a main parameter for the first method and gelatinization for the second one [87].

The solvent casting method involves a three steps process: solubilization of raw materials in a suitable solvent, casting of the obtained solution, respectively drying of casted solution under proper conditions; each step parameter influences the intermediate and final products, the main advantage being low-cost film manufacturing without a specialized equipment. However, due to multiple operation conditions, this method present several bottlenecks: the proper choice of the solvent—solvents must be non-toxic, as there it



remains a possibility that the solvent can impurify the polymer and to negatively affect the active substances characteristics; the proper choice of the molds—for food industry, the mechanical characteristics of the obtained films must permit molding on different types of products; extra time for drying into the molds—slows down and makes the process more expensive; proper temperatures for drying—the process must be optimized for proper temperatures in order not to damage the films and final products, which often degrades at higher temperatures [88,89].

Extrusion methods are in use at industrial scales for obtaining polymeric coating films, but they involve the use of specialized equipment and supplementary materials, such as plasticizers and stabilizers. Through thermomechanical processes such as extrusion, injection, kneading, and casting, different films can be obtained [90], a proper choice of the added plasticizer influencing the physicochemical properties of the final material, decreasing hydrogen bonding between polymers, and increasing intermolecular spacing. For example, hydrophilic plasticizers such as protein hydrolysates can enhance water vapor permeability levels of the vegetal based films, having a double role: plasticizer and active ingredient [91].

Moreover, for extrusion methods, a major challenge is maintaining a balance in choosing the suitable equipment operation parameters and proper plasticizers and stabilizers, this balance being a key point for obtaining coating materials with specific physico-chemical characteristics (homogeneity, shear rate, shear stress, and residence time control). An example of choosing proper conditions is the study of Sun et al. [92]. The authors developed starch/polyhydroxyalkanoate films through extrusion method using as cross-linking agent, citric acid, adipic acid, boric acid, and borax, at a blending and compounding screw speed of 60 rpm, and film blowing screw speed of 30 rpm. The obtained films proved to have the best properties (high tensile strength (9 MPa) and elongation at break over than 60%) for the above presented operations conditions, only when the citric acid and adipic acid were applied.

The extrusion method for obtaining coating materials is used at industrial levels with high performance and low costs [93]. The disadvantage of this method is mainly related to the processing temperature when the raw material is based on more than two components, as all the components must have similar melting points.

The nature of food products considered, surface properties, and final targeted application (such as protective packing, antibacterial, enhancing nutritional value, etc.) leads to the selection of the deposition method (Table 3).

**Table 3.** Coating materials for food industry.

Coating Material	Food Product	Obtaining Method for the Coating Material	Coating Method	Coating Properties	Ref.
Coating materials for fruits					
Papaya - <i>Moringa oleifera</i> leaf powder	Pear	Solvent casting	Food packaging films	Controlling physicochemical properties; antioxidant activity	[89]
Chitosan	Strawberries	Solvent casting	Drop-casting, films for packaging	Controlling physicochemical properties; antimicrobial activity	[94]
Chitosan	Blueberries	Solvent casting	Dipping	Controlling physicochemical properties; antimicrobial and antioxidant activity	[95]
Pea starch/Guar gum	Oranges	Solvent casting	Spraying	Controlling physicochemical properties and fruit quality assessments	[96]
Chitosan/Nisin/SiO <sub>2</sub> nanoparticles	Blueberry	Solvent casting	Dipping	Maintaining nutritional values of the fruits during storage	[97]

Table 3. Cont.

Coating Material	Food Product	Obtaining Method for the Coating Material	Coating Method	Coating Properties	Ref.
Coating materials for vegetables					
Calcium caseinate	Carrots	Solvent casting	Casting	Prolonged shelf-life and antimicrobial activity	[98]
Alginate/ <i>Aloe vera</i> gel/ $\text{TiO}_2$ nanoparticles	Tomatoes	Solvent casting	Dipping	Prolonged shelf-life and antimicrobial activity	[99]
Chitosan/cinnamon essential oil	Cucumber	Solvent casting	Dipping	Controlling <i>Fusarium solani</i> fungal growth	[100]
Chitosan/melatonin	Cucumber, broccoli	Solvent casting	Dipping	Antioxidant and antimicrobial properties	[101]
Coating materials for dairy products					
Gellan/xanthan/k-carrageenan/ <i>Aloe vera</i> gel	Cheese	Solvent casting	Dipping	Inhibition of <i>Penicillium roqueforti</i> fungal growth	[102]
Starch/glycerol/natamycin/nisin	Gouda cheese	Solvent casting	Dipping	Barrier against external contamination ( <i>L. innocua</i> and <i>S. cerevisiae</i> )	[103]
Chitosan/ZnO nanoparticles	White brined cheese	Solvent casting	Dipping	Controlling <i>E. coli</i> fungal growth	[104]
Coating materials for meat products					
Alginate	Sausages	Extrusion	Dipping	Prolonged shelf-life up to 8 weeks	[105]
Chitosan	Chicken meat	Solvent casting (enhanced with plants extract)	Active films for packaging (wrapping)	Films for lipid oxidation and decrease microbial count	[106]
Gelatin/poly (lactic acid) epigallocatechin	Fried fish	Solvent casting, compression, molding, lamination	Layer-by-layer films, bags	Prolonged antioxidant activity during storage (30 days)	[107]
Gelatin/chitosan/gallic acid/clove oil	Salmon	Solvent casting	Dipping	Preserve fresh salmon fillet during cold storage extending shelf-life and antimicrobial properties	[108]
Chitosan/tomato extract	Pork loin	Solvent casting	Dipping	Enhanced physicochemical antimicrobial and antioxidant properties	[109]
Coating materials for other foods packaging					
Triticale flour films	Cherry tomatoes	Solvent casting	Active packaging boxes	Controlling physicochemical properties	[110]
Starch/ <i>Ilex paraguariensis</i> extract	Market potential packing	Extrusion, compression molding	Active packaging	Active and smart materials to replace the use of conventional plastic	[111]
Starch/gelatin-beeswax	Potential packing	Extrusion	Active packaging	Active materials to replace the use of conventional plastic	[112]
Chitosan/guar gum/ZnO	Potential packing for cheese	Solvent casting	-	Controlling antimicrobial and organoleptic properties	[113]
Cassava starch/anthocyanin	Potential packing	Extrusion	Smart packaging	pH change indicator for meat stored at 6 °C	[114]

The enhancement of the final properties can be obtained by the addition of different ingredients into the coating material. Glycerol, for example, can increase the elasticity and the hydrophobic character of chitosan-based films used as protective layer for strawberries, maintaining the bactericidal character after the plasticization [94]; by the addition of procyanidins, it can be modified the antiradical activity and decreased the microbial growth, thus prolonging the shelf life [95]. Before immersing the products into the coating material, disinfectant solutions (sodium hypochlorite) are used. Due to the hydrophilic nature of pea starch and guar gum, Saberi et al. used as a coating material a mixture with hydrophobic compounds (shellac and oleic acid), obtaining lower levels of respiration rates in coated fruits (approximately  $8 \mu\text{g}/(\text{Kg} \times \text{s})$ ) [96]. This represents the capability of

the coating to modify the internal atmosphere of the fruit as a protective gas barrier, the materials being better candidates than the commercial products, where levels of respiration are higher ( $12.8 \mu\text{g}/(\text{Kg} \times \text{s})$ ). For coating the blueberries, the properties of the chitosan films were enhanced through the addition of nisin and silicon dioxide nanoparticles, by Eldib et al., thus obtaining a good control of shrinking (38.52%) and decay rates (8.61%), as well as the maintaining of main nutritional parameters (Vitamin C—7.34 mg/100 g and polyphenoloxidase—558.03 U/(min  $\times$  g)) [97]. Additionally, the irradiation treatment can enhance the mechanical properties of the coating material. This is the case of calcium caseinate  $\gamma$ -irradiated with a dose of 32 kGy and a low-dose of  $\gamma$ -irradiation post-treatment of 0.5 kGy [98]. In the experiment was observed an improvement of the mechanical and water vapor barrier properties of the materials for prolonging shelf life of carrots during storage. The total mesophilic flora (*Enterococcus faecium*, *Escherichia coli*, *Listeria monocytogenes*, *Pseudomonas aeruginosa*, *Salmonella typhimurium*, and *Staphylococcus aureus*) decreased after only one treatment cycle (3.2 log CFU/g compared to 5.4 log CFU/g in control) and the bioactive cross-linked coating proved to be a good alternative to be used as a natural treatment.

The properties of the coating materials can be also improved by using natural polymers in nanostructured forms. Due to the particle size, nanostructured chitosan (with particle size of 5 and 8 nm) and chitosan functionalized with cinnamon essential oil (particle size 4.34 nm) have the ability to increase total chlorophyll content at the end of storage time (from 6 mg/L for control sample to 14 mg/L for treated sample) and successfully inhibit fungal growth (from 600 CFU/10g tissue for the control sample to less than 100 CFU/10 g tissue for the treated sample—tests applied for *F. solani*) [100]. Dimensions of particles and antibacterial effect of cinnamon essential oil are responsible for the obtained results on cucumber samples. Additionally, metallic oxides nanoparticles having a higher surface area to volume ratio are able to damage the cell membrane through penetration into the bacterial cells [104].

Besides nanotechnology products, coating materials can be used for the residues generated from the agro-industrial sector, which nowadays produce increased amounts of residues [106]. Serrano-León et al. developed and characterized active packaging based on peanut skin and pink pepper residue extracts incorporated in chitosan, in order to evaluate their effects on lipid oxidation and antimicrobial effect on chicken products [106]. The antimicrobial activity of chitosan, conferred by the presence of amino groups, was potentiated by the extracts' antimicrobial properties, leading to an enhanced effect. Moreover, the antimicrobial effect of polymeric coatings enriched with natural products can be enhanced through its casting procedure. Lamination can improve the performance of polymeric films by combining the properties of different films into one sheet, its different layers having specific properties, such as moisture resistance and mechanical stability, or gas barrier [107]. Additionally, by adding natural extracts from fresh vegetables into polymeric coatings, due to changing a variety of factors, such as molecular weight, concentration, viscosity, deacetylation grade, it can be prolonged the shelf life of meat products [109].

Coating materials are an interesting domain and the concept of active packaging gained new valences, offering the possibility of interaction among the food product, the packaging, and the environment, new smart packaging systems based on natural products being developed in order to improve the quality of food products, thus prolonging their shelf-life [110–114].

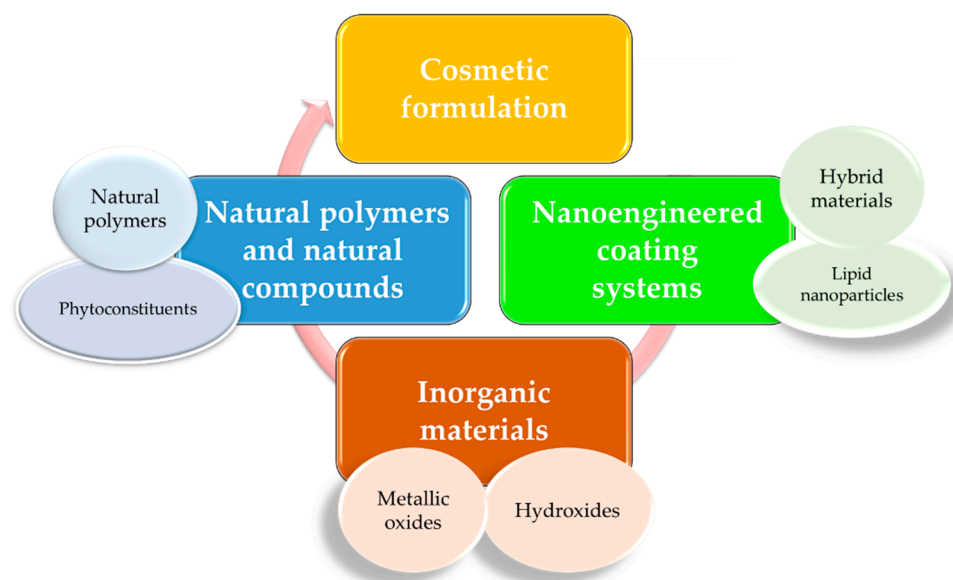
The deposition methods are dependent on the nature of food that should be coated, the support surface being a main parameter for a successful coating [4]. Additionally, surface tension, density, and viscosity of the coating material influence the selection of applying methods and equipment used. Dipping and spraying technologies are usually used as application methods of coating materials for the fresh products, ensuring uniformity across a rough and complex shape. In the case of spraying method, several shortcomings are mainly related to the working parameters of the equipment, which must be corroborated with the coating's physico-chemical properties [115]. For a low-density coating material,

fluidized-bed processing is the method of choice, and in confectionery sector, panning method is used to apply thick layers to hard materials.

### 3.2. Cosmetic Industry

For coating systems used in cosmetic formulations and pharmaceutical industry, the approach is different than in the above discussed sections dedicated to medical devices or food industry. The subject is very vast, and itself can be a topic for a review paper, but some interesting examples of coating materials and active substances will be discussed. The development of new coating delivery systems in cosmetic formulations and pharmaceutical industry, nowadays follow concerns regarding the use of green technologies and non-toxic environmental materials. Developing cosmetic formulations is a significant challenge as there can appear diverse bottlenecks, the final target efficacy (sun screen protection, antiaging, antiwrinkle, etc.) being dependent on the vehicle formulation, choice of emulsifiers, solvents and emollients.

Different types of nanoengineered coating systems (e.g., liposomes, niosomes, transferosomes, lipid nanoparticles, core-shell materials), polymeric microparticles, nanoparticles, inorganic materials, etc., have been successfully used in cosmetic formulations, improving the penetration of active substances into the skin (Figure 3).



**Figure 3.** Potential coating materials for cosmetic formulation.

For cosmetic formulations, the requirements are different than for a topical pharmaceutical preparation, many factors influencing the properties of the final products. The coating material of the active substance must be compatible with the oil-water emulsion, water-oil emulsion or double emulsion in the case of cosmetic formulations [116].

#### 3.2.1. Lipid Nanoparticles

Cosmetic formulations can present some limitations due to their requirements such as higher absorption, low washability and good stability, so different nanocarriers were proposed. Liposomes can entrap hydrophobic molecules, have low toxicity, can be easily prepared and have the ability to extend product shelf life, having the main disadvantage of rapidly releasing water-soluble active substances [117]. Niosomes, transferosomes, and ethosomes are used both in cosmetic and pharmaceutical industry, overcoming the liposomes limitations, due to producing costs and manufacturing procedures [118]. These particles must possess high encapsulation efficiency and long-term stability. Enhancing the adhesion of carrier particles to the skin and control the release of active agents over a period

of time can be achieved using different polymers, such as poly(3-hydroxybutyrate) [119]. To overcome the drawbacks related to the lipid composition or the rigidity of the liposome's membrane, polysaccharides can be used as a coating layer, being more resistant in the presence of surfactants and electrolytes, compared to the non-coated materials [120].

Lipid nanoparticles are widely applied in cosmetic formulation as core-shell materials, in order to protect the active ingredients. The advantages of using these systems are based on their ability to incorporate both lipophilic and hydrophilic compounds, allow released control, as well as their preparation process, which do not involve organic solvents; among this category, the nanostructured lipid carriers (NLCs) present an increased loading efficiency of actives compounds, compared with solid-lipid nanoparticles (SLNs) [121]. Nanostructured lipid carriers (NLCs) loaded with azelaic acid, white willow bark extract and panthenol were used for improving the reconstruction of epidermal cells, antioxidant NLCs inhibiting 97% of short-life radicals and 15% of ABTS long-life radical cations [122]. A hydration effect (up to 74%) and a skin elasticity reaching 90% were obtained after the topic application of carrot and marigold extract encapsulated in NLCs based on rosehip oil or black cumin oils [123]. Hybrid nanoparticles, composed of lipids and silica, were developed by Andreani et al., in order to be loaded with UVB filter, octyl methoxycinnamate [124]. Encapsulation efficiency of 98.3% and a SPF (sun protection factor) value of 10.62 was obtained for particle dimensions of  $210.0 \pm 3.341$  nm, while no irritation effects on the HET-CAM test (Hen's egg-chorioallantoic membrane test) were observed for the developed materials. The main drawback of using SLNs and NLCs as coating for active substances in water based cosmetic formulations is aggregation and gelation of particles, which causes instability of the developed systems; however, between the two solutions, NLCs are preferred for use in cosmetics, due to adhesiveness, skin penetration enhancement, occlusion, lubrication and skin hydration [125]. Similar to liposomes, the modification of NLCs' surface with natural polymers (non-toxic, biodegradable and biocompatible) will prevent their aggregation through the repulsion of positive charges [126].

### 3.2.2. Hydroxides and Oxides

Layered double hydroxides (LDH) are clays based on a hydrotalcite structure, of natural origin, for which the Van der Waals forces (hydrogen bonding) hold the stacked layers together [127]. They possess a host-guest type structure, having the ability of coating different active molecules, as a result of the possibility to tune their crystallinity, texture and structural properties [128–130].

Additionally, from the category of inorganic coating,  $\text{TiO}_2$  and  $\text{SiO}_2$  nanoparticles are reported due to their stability and non-toxicity as platforms for active substances delivery and theranostics at certain dimensions.  $\text{TiO}_2$ - $\text{SiO}_2$  core-shell nanoparticles with  $\text{TiO}_2$  dimensions of 100 nm proved to have efficiency towards the development of cosmetic products (UVA protection factor 39 and sun protection factor 42), in the study of Swain et al. [131], while at smaller dimensions (10 nm) they do not exhibit such properties [132]. Metallic oxides can be used as coating material for other metallic oxides, or for organic active substances. The cytotoxicity of  $\text{TiO}_2$  nanoparticles, which are usually used for their photocatalytic properties (being an efficient absorber of UVA and UVB), can be reduced by the use of an adequate inorganic coating, such as nanocomposites based on  $\text{Fe}_2\text{O}_3/\text{CeO}_2$  or  $\text{Y}_2\text{O}_3$ , which can promote cell viability and proliferation [133,134]. Hydrophilic fumed  $\text{SiO}_2$  nanoparticles can cover  $\alpha$ -leucine using ultrasonic irradiation in high-pressure liquid carbon dioxide, thus obtaining a potential cosmetic formulation, acting as modifier for low water soluble active compounds [135]. As a future trend, silica nanoparticles modified to achieve different hydrophobicity can be used in formulation of Pickering emulsions, in order to obtain novel cosmetic products at industrial level [136].

### 3.2.3. Natural Polymers

Due to the ability of natural polymers to enhance the physicochemical properties of the cosmetic products, these are successfully used as rheological modifier, water-

soluble binders, thickeners, film-forming agents, conditioners or texturing and hydrating agents [137]. Moreover, comparing to food industry where natural polymers are usually used as coating materials, providing a controlled release of active ingredients, for cosmetics applications these polymers can act themselves as active compounds [138] or can protect active ingredients of chemical self-degradation/oxidation, as in the case of  $\beta$ -cyclodextrin [139].

#### 3.2.4. Phytosynthesized Metallic Nanoparticles

In the last decades, nanotechnology has offered a series of valuable tools for improving our daily life, important aspects being related to the cosmetic industry [83]. The ability of plants extracts to mediate chemical reduction of metallic salts, leading to the formation of phytosynthesized metallic nanoparticles, proposed as potential agents in multiple applications, offering a viable alternative to the use of environmentally hazardous reagents [140]. Phytoconstituents act as reducing agents in the obtaining reaction, and moreover they continue their role, as coating agents for the nanoparticles. Thus, it is offered a synergism between the compounds towards enhanced properties and against agglomeration and aggregation [141]. Silver and gold phytosynthesized nanoparticles can be used in cosmetic formulations, due to their free radical scavenging activity, reductive and anti-lipid peroxidation properties, as well as to their anti-aging properties, which some authors assigned to the presence of phytoconstituents coating [142–144]. Phyto-mediated Zn and ZnO nanoparticles can be used as protective agents against UV rays, also possessing antimicrobial and antioxidant properties [145,146].

Combined with the advantages of using natural phytoconstituents, the use of this type of nanoparticles represents a valuable raw material in the cosmetic field, but still needs future research regarding obtaining methods and toxicological aspects.

#### 3.3. Coatings for Miscellaneous Applications

Different types of pollutants are produced nowadays in large amounts due to a rapid increase in the world population and widespread industrialization, so the development of new materials for environmental remediation represents a goal of utmost importance [147]. Advanced oxidation processes (AOP) are by far the most applied methods for removing hazardous compounds from water. Catalytic ozonation represents an AOP process with high efficiency in the application on effluents with a low and average flow rate and pollutants concentration [148]. The optimization of this process, in order to achieve better performances is very difficult and requires multiparametric monitoring of oxidation reaction, the catalyst playing a main role. In the last decade, numerous materials and technologies were proposed for a better and complete oxidation processes. In porous structures, nanoparticles are formed inside pores as a result of a multistep, costly and difficult process without having a very good control over their chemical composition, dimensions, and shape [149].

An interesting alternative is represented by the immobilization of catalyst in the form of thin-films coatings using different substrates (glass, quartz, polymers, textile materials, etc.), according to their uses, having the advantage of being cost effective and easily recycled after washing [150,151]. Thin film morphology containing phytosynthesized metallic or metal oxides nanoparticles gained more attention in the last decades, being suitable for catalytic processes, since this approach includes advantages of using nanoparticles and avoid the diffusivity problems (in fixed bed systems) or daunting separation step (in slurry approach). Another innovative and eco-friendly aspect of this type of materials consists in the preparation of novel thin-film catalysts using plant extracts, without harmful substances [152,153]. Additionally, phyto-mediated metallic or metal oxide nanoparticles can act as catalysts themselves (being coated by the phytoconstituents), or be included in nanocomposite materials for the catalytic reduction of organic dyes [151,154,155], or can be coated by natural minerals, such as perlite [156].

For other environmental applications, coating materials based on natural product can be successfully applied. This is the case of sensors developed using silver nanoparticles coated with natural polymers, such as xylan, which are able to detect  $\text{Hg}^{2+}$  at a 4nM detection limit [157] or natural minerals such as  $\text{Cs}_2\text{SnI}_6$  perovskite used for coating ZnO nanorods for solar cells [158]. Coatings based on rhamnolipid biosurfactant, gum karaya and xanthan gum are able to inhibit the agglomeration of nanoparticles, such as zero valent iron nanoparticles, in order to be used for organic and inorganic bioremediation [159–162]. For soil remediation applications, coating layer has a double role: protect the inorganic core against agglomeration and percolate into the spaces between soil particles in order to travel longer distances before being trapped by the soil matrix [163].

Environmental factors affect not only the human health, being able to damage important cultural heritage objects which are kept in outdoor conditions. The use of protective coatings gained importance in heritage conservation, and coatings based on natural products replace successfully chemical hazardous substances [164]. From the category of inorganic compounds, calcium hydroxide can be used as a coating material, due to its property to be transformed under natural atmospheric conditions into a hard coating of insoluble  $\text{CaCO}_3$ . Moreover, when  $\text{Ca}(\text{OH})_2$  is applied in its nanoparticle state, the deposition and penetration of prepared suspensions through external porous of the surface are enhanced. Daniele and Taglieri reported the efficiency of consolidation with this type of coating more than 75% for stone samples [165], while Lanzón et al. reported that nanoparticles with dimensions in the range 200 to 600 nm can penetrate through conventional pores of mechanically weak materials (lime mortars), this type of coating being used for the consolidation of deteriorated walls of the Roman Theatre of Cartagena [166]. Despite the disadvantages (160 repetitions) presented by Slízková et al. [167], the use of alcohols as dispersion media can overcome the drawbacks of a large number of applications of the coating material [166].

As a very interesting aspect regarding the potential use of natural resources for the development of next-generation materials for highly specialized scientific, medical or precision equipment, the biomachining process can be mentioned. It represents the metal processing using lithotrophic (usually extremophile) bacteria, as an intermediate step, before applying the final functional coatings. An example on this topic is the work of Díaz-Tena et al., presenting the application of *Acidithiobacillus ferrooxidans* for biomachining oxygen-free copper, resulting in a finished and/or engraved material surface, without the shortcomings of traditional processing methods [168].

For wooden cultural heritage objects, the appropriate materials for coating layers are natural products, such as proteins, lipids, polysaccharides, or terpenoids, having a waterproofing role and, occasionally, as ingredients of binding media [169], while for iron artefacts, adding natural compounds (tannins) into commercial resins can inhibit their corrosion [170]. For conservation studies, natural polymer coatings are preferred instead of resins, for indoor objects, due to their water-solubility, thus avoiding the use of harmful solvents, necessary for the application and removal of commonly used commercial protective coatings. Giuliani et al. used a coating based on chitosan, which acted as a reservoir for the inhibitors benzotriazole and mercaptobenzothiazole, for bronze artefacts, contributing to the formation of a barrier layer, thus improving the protective properties of the treatment [171].

Conservation methods based on the chemical strategies of using natural coatings can be adapted for paper artefacts, too. Jia et al. obtained an antibacterial and antifungal composite material based on ZnO/cellulose nanocrystals, and the chemical and mechanical properties of coated papers after dry heat and UV accelerated aging were measured, in order to demonstrate the efficiency of the treatment [172], the cellulose layer having a good compatibility and affinity with paper cellulose fibers. The treated papers had higher thermal and UV stability and exhibited an inferior loss of strength. For papers coated with chitosan nanoparticles, the protection is due to the formation of chitosan protective layer when the nanoparticles combined with  $\text{H}_2\text{O}$  and  $\text{H}^+$ , the deacidification of the paper being

produced (a pH increase from 5 to 7 being recorded), also increasing tensile strength and folding endurance [173].

#### 4. Conclusions and Future Perspectives

The rapid technological developments from recent decades has led to an exponential increase of theoretical findings and practical development of new materials used as coatings for different applications, mainly based on their refined properties; however, all these materials have their own shortcomings and restrictions in application: for medical application, the development of controlled release strategies for active substances is necessary, in order to optimize the therapeutic effects of the treatment; for food industry, edible coatings have great potential to extend the shelf life of products, recent advancements in the field proposing new plant-based materials or nanotechnology products, future research being necessary for their industrial application and maintaining the laboratory characteristics of the materials; for cosmetic industry, materials' limitations due to their specific requirements, such as higher absorption, low washability, and good stability, must be overcome.

Regardless of application, future studies are also needed, in order to obtain optimized layer-by-layer or smart coatings from natural products, with a fine tuning of their properties to a phase transition triggered by temperature changes or by presence of selected chemical species, especially in the case of multiple components, which can be used and tailored to adapt to any kind of protection. In all cases, special attention must be attributed to mechanical properties of the coating material, which require an equilibrium between resistance and elasticity.

The application of coating technologies to develop new approaches is limited and correlated with their application, as a result of the complexity of the coating process, physical and chemical issues, the difficulty of achieving uniform coatings based on natural compounds, the diverse properties of different support materials, as well as due to the production cost, which sometimes does not meet the requirements for large-scale production. Further developments may facilitate an optimal use of natural compounds as coating materials using modern techniques with a lower consumption of solvents, time, and energy.

This review paper summarized different aspects of the use of natural products as functional coatings for various applications, highlighting their importance in the production of coatings as they have the advantage of enhancing the physical and chemical properties of the products. In the context of green chemistry, in which the use of substances with less negative effects is mandatory, natural functionalized coatings are potential candidates, not only for the above-described applications, but for others, such as agriculture or for advanced sensors, smart materials and nanotechnology.

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