Encapsulated Natural Bioactive Compounds in Food Industry

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Definition

Plants are the most abundant bioresources, providing valuable materials that can be used as additives in polymeric materials, such as lignocellulosic fibers, nano-cellulose, or lignin, as well as plant extracts containing bioactive phenolic and flavonoid compounds used in the healthcare, pharmaceutical, cosmetic, and nutraceutical industries. Bioactive packaging is developing to additionally provides antibacterial and antioxidant activity with the same goals i.e., extending the shelf life while ensuring safety of the food products. New solutions are designed using natural antimicrobial and antioxidant agents such as essential oils, some polysaccharides, natural inorganic nanoparticles (nanoclays, oxides, metals as silver) incorporated/encapsulated into appropriate carriers in order to be used in food packaging. Electrospinning/electrospraying are receiving attention as encapsulation methods due to their cost-effectiveness, versatility and scalability. The electrospun nanofibers and electro-sprayed nanoparticles can preserve the functionality and protect the encapsulated bioactive compounds (BC).

1. Introduction

Pristine polymeric materials alone often show poor physico-chemical properties. The incorporation of additives into polymeric materials improves their processability, tuning their properties to make them suitable for multiple applications like packaging, automotive, design, constructions, etc. Additives of various compounds or nanoparticles to the virgin polymers can improve both bulk and surface properties of the products. According to the European Community, an additive is “a substance which is incorporated into plastics to achieve a technical effect in the finished product, and it is intended to be an essential part of the finished article” [1]. Efforts are made to incorporate various biodegradable additives with a low environmental fingerprint, such as by-products and biomass. Therefore, biobased, biodegradable polymer composites are more and more studied, as a large number of biodegradable polymers are already commercially available [2].

Composite materials exhibit advantages from the combination of multiple properties, which cannot be achieved by a monolithic material as they are systems which consist of one or more discontinuous phases enclosed in a continuous matrix [3]. The discontinuous, disperse phase, which is completely immiscible with the matrix, can be a reinforcement (reinforcing agent) or filler and the resultant composite shows optimized mechanical properties, such as strength, stiffness, and hardness [4]. As traditional plastics are resistant to biodegradation, the concept of using natural plastics (natural biodegradable polymers or biopolymers) as reinforced matrices for biocomposites is getting more and more interest.

Packaging is used to protect foods from environmental factors and microbial contamination to maintain food quality and safety [3]. Food spoilage or poisoning directly affecting public health can be reduced through bioactive packaging, which extends the shelf life of perishable food particularly those susceptible to microbial alteration [5].

Unlike modified atmosphere packaging where the role is only to restrict exchanges of CO2, O2, water vapor, and aromatic compounds between the food and its external or local environment [2], bioactive packaging provides antibacterial and antioxidant activity with the goal of extending shelf life and the safety of food [8]. The development of active/bioactive materials aiming to maintain or enhancing the safety and quality of packaged food by the incorporation of antimicrobial natural compounds and/or antioxidant natural compounds [9] is now an active research area [10][11][12][13][14]. Unfortunately, their use in natural form in food packaging materials in foods is restricted because of their low stability against temperature, oxygen, or light exposure during processing of the food, distribution, and storage [15]. Also,
their uncontrolled release profiles can significantly deteriorate their biological benefits \(^{15}\). To overcome these limitations, appropriate carriers and encapsulation techniques were designed. The natural bioactive compounds (BCs) with antimicrobial and antioxidant activities as essential oils, some polysaccharides \(^{16}\)[17], natural inorganic particles (oxides, nanoclays, metals, such as silver) \(^{18}\) into food packaging can protect food from microbial alteration and extend shelf life, reducing economic losses and health issues caused by foodborne pathogens \(^{19}\)[20].

2. Classification of Biodegradable Polymers and Natural Additives

Natural additives can be high molecular weight (natural polymers), such as proteins (collagen, silk, and keratin), carbohydrates (starch and glycogen), cellulose, lignin, high molecular weight phenolics (tannins and derivatives), and low molecular weight active substances, such as cold-pressed oils, essential oils (organic volatile compounds, generally of low molecular weight, containing phenols, alcohols, ethers or oxides, aldehydes, ketones, esters, amines, amides, heterocycles, and terpenes \(^{21}\)), or low molecular weight phenolics (phenolic acids and flavonoids) \(^{22}\). Natural additives are widely used materials in many applications in combination with synthetic or natural polymers. These materials, together with pomaces and biowaste, are nontoxic, less expensive than the synthetic ones, ecologically friendly, and widely available. The natural polymeric additives and fibers can be classified according their origin into polymers extracted from biomass or produced by micro-organisms, or obtained from vegetable (plant), animal, or mineral sources \(^{23}\)[24]. Biopolymers that are biobased and bio-degradable include polyactic acid (PLA), polyhydroxyalkanoates (PHA: Poly(3-hydroxybutyrate) (PHB), poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV), and poly(3-hydroxybutyrate-co-4-hydroxybutyrate) (PHBHB)) derived mainly from microorganisms and thermoplastic starch (TPS)-based materials. Aliphatic polyesters are also used because of their biodegradability and include poly(glycolic acid) (PGA) and poly(alkylene dicarboxylates) (such as poly(butylene succinate) (PBS) and poly(butylene adipate-co-terephthalate) (PBAT)), derived from both fossil fuel and renewable resources \(^{24}\). Natural polysaccharide biopolymers (such as chitosan/starch/alginate) are nontoxic, biodegradable, biocompatible, and largely used in food packaging: Chitosan is known for its broad antimicrobial activity and its excellent film-forming properties; alginates have good film-forming properties, retain moisture, reduce microbial counts, and retard oxidative off-flavors; and starch is also particularly important for its cheap price and its frequency in nature. Mineral and animal fibers such as hair silk and fibers are not widely used as reinforcements - but plant fibers have been used widely in biocomposites field for applications in the areas of automotive, marine and construction \(^{25}\). The most interesting fibers for composite reinforcements and most commonly accepted fibers by the industry \(^{26}\) are from plants, in particular bast, leaf, and wood fibers. The fibers are basically a rigid, crystalline cellulose microfibril-reinforced amorphous lignin and/or hemicelluloses matrix. As the environment is concerned, these fibers are biodegradable, light weight, relatively cheap, and are “carbon positive” since they absorb more carbon dioxide than they release. In thermoplastics they are introduced by melt mixing and in thermosets by vacuum-assisted transfer molding (VARTM) and vacuum bag resin transfer molding (RTM) \(^{27}\).

Summarizing the applications of the most-used natural polymers and natural extracts as components/additives in new high performance materials, based on their source and type (animal/vegetable/mineral and low/high molecular weight), natural additives are widely used as filler and additive materials to improve the biodegradability or the mechanical properties (reinforcements) or to provide antioxidant or antibacterial activity in various synthetic or natural polymeric matrices.

3. Encapsulation

Essential oils (EOs) and other active compounds, in natural form, have restricted applicability \(^{28}\) because of their poor stability, as they are easily degraded \(^{29}\) by oxidation, hydrolysis, crystallization or enzymatic deterioration, during storage or processing in harsh conditions in the presence of oxygen and light \(^{30}\). Also, it is important to consider that these active compounds have low thermal stability, since high temperature used during food processing causes loss of their functionalities \(^{31}\). This can significantly deteriorate their flavor, solubility and biological benefits as is the case with the pomegranate peel extract which is currently affected by color and instability issues associated with easy oxidation \(^{32}\).
or the EO of *Satureja hortensis* which drastically changes its composition through the heating of the samples over 160 °C [33]. Also, volatility [28] and low water solubility [34] are associated with the EOs when exposed to air, which limits its application in food preservation [35]. The strong and intense flavor of EOs may be transferred as taste to the packed food [36][37] as well. For these reasons, a protection technique is required before the addition of natural EOs (or other BCs) into food systems [38]. Consequently, many researchers have encapsulated them into other protection materials in order to make full use of their anti-oxidant and antimicrobial properties [39].

The research developments in the area of the nanoencapsulation of BCs in food packaging materials are continuously growing [40] as the nanoencapsulation [41] can protect the BCs against oxidative degradation upon exposure to air or high temperatures during food processing [42], and can enhance the bioavailability of the BC, releasing them in a controlled manner and preserving their activity [43]. For example, encapsulating thyme EO into β-cyclodextrin/ε−polylysine can reduce undesirable deficiencies such as volatility and hydrophobicity of the BCs [44]. The antimicrobial carvacrol can be protected/encapsulated in a starch fiber matrix, to avoid direct contact with food and reduce the effects on sensorial features [45]. Encapsulation in zein microparticles improved thermal stability of polyphenols from maqui fruit extract when exposed to high temperatures related to processed foods [46]. Orange and thyme oil adsorbed in halloysite or montmorillonite clay and then encapsulated in a polyethylene/polyamide/polyethylene multilayer film prolonged aroma release [47]. Encapsulation of black pepper (*Piper nigrum* L.) EO into sodium alginate and gelatin by complex coacervation avoid the loss of the main volatile from EOs which were preserved (80% of their original content) [48].

There are several methods to encapsulate/protect these sensitive natural bioactive antioxidants/antibacterials (including phenolic compounds, etc.) in food packaging for active compound delivery: films [49][50][51], microencapsulation via the spray-drying (wall materials that suitably protect the inner EOs from oxidation and evaporation) [52], nanoprecipitation [53], but recently, electrohydrodynamic processes [54] “electrospinning” [55] and “electrospraying” [56][57] have received increased attention due to their versatility, cost-effectiveness, and scalable technologies [58][59][60][61].

### 4. Encapsulation by Electrospinning

A typical electrospinning set-up has a high voltage power supply connected to a metallic nozzle and a metallic collector. When a high voltage is applied between the solution of the polymer and a metallic collector, a drop of a polymer solution ejected at the tip of the nozzle will turn into a conical droplet known as the Taylor cone (Figure 1a), the electrostatic repulsive force acting on the drop surface counteracts the surface tension and a liquid jet is ejected that is deposited onto the collector in the form the nanofiber mesh [62]. Electrospinning and electrospraying can operate at ambient conditions (atmospheric pressure and room temperature) producing micro/nanostructures in dried form in a one-step process [63]. The viscosity of the solution is the dominant parameter which decides if fibers (electrospinning) or droplets (electrospraying) will be obtained (Figure 1b). A too low viscosity results in droplets of polymer (electrospray) due to the interruption of polymeric filaments. The boundary concentration between electrospray and electrospinning depends on the molecular weight of the polymer and the nature of the solvent [64].
The needle electrospinning is inexpensive and versatile but its use in applications is restricted because its low production rate. Also, the needle blocking frequently occurs, particularly with high viscosity polymer and functional nanoparticles/bioactive substances in the spinning solution, which makes it difficult to produce nanofibers continually. Therefore, the needleless electrospinning was developed for mass production of nanofibers. During needleless electrospinning the polymeric multi-jet initiation is a self-initiated process taking place on a free liquid surface and usually rotating disks/cylinders are used to feed the initiated Taylor cones with polymeric solution to keep the electrospinning process continuous and not interrupted. A profiled multi-pin electrospinning setup may overcome the limitations of the needleless and needle electrospinning (for example uncontrolled/uneven Taylor cone formation, needle clogging, and the requirement of very high voltage). A profiled multi-pin surface is designed to support the nano/microparticles in the polymer solutions. This increases the range of multifunctional electrospun nanofiber applications by the development of a single matrix with multifunctional characteristics and improved mechanical and electrochemical performances. The most common approaches used to encapsulate bioactive antioxidants/antibacterial into nanofibers are emulsion and coaxial electrospinning. In both cases the nanofibers generated have an outer polymeric sheath (base polymer) and inner bioactive core, although the processes involved are different: coaxial electrospinning generates core–sheath fibers by physical separation of two polymeric solutions flowing through concentrically aligned nozzles: an outer sheath polymeric solution and the second inner polymeric solution containing the bioactive substance. The emulsion electrospinning involves a single polymeric solution containing an emulsion of the bioactive substances; the subsequent separation of the emulsified droplets into the sheath polymeric phase takes place as the solvent evaporates from the electrospun fibers.

The obtained electrospun nanofibers and electrosprayed nanoparticles can serve as protection for the bioactive compounds against any severe conditions (such as high temperatures and/or pressures involved during packaging or food processing, storage, light, oxidation) preserving the functionality of the active compound encapsulated within the electrospun nanofibers as well as controlled delivery/release of bioactive compounds. Their efficiency in maintaining the stability of the bioactive compound enhances the bioavailability and bioactivity during processing, storage and consumption, the encapsulation process alleviating the unpleasant flavor or taste of phenolics.

For food packaging, the electrospun/electrosprayed nanofibers/nanoparticles can be more efficient than films in view of several advantages such as larger surface to volume ratio, higher crack resistance,
interconnective structure, good adhesion properties (in case of coatings) and higher porosity, high loading capacity of the active compounds \(^{75}\).\(^{76}\).\(^{77}\).

Using this approach, new packaging can be formulated in a single step with the additional advantage of simultaneously and intrinsically producing interlayers \(^{78}\).\(^{79}\).\(^{80}\) (coatings \(^{81}\)) with encapsulation performance \(^{82}\). This offers several benefits compared to the traditional encapsulation techniques which may be detrimental for the active properties of many of the antimicrobials and antioxidants (EO) due to the high temperatures used for drying the obtained materials \(^{83}\).\(^{84}\).

Compared to the traditional encapsulation techniques which may be detrimental for the active properties of many of the antimicrobials and antioxidants (i.e., EO) due to the high processing temperatures used for drying the obtained materials \(^{83}\).\(^{84}\) electrospinning offers the advantage of the absence of heat \(^{71}\).\(^{72}\).\(^{73}\).\(^{74}\) during the drying of the structures. As the solvent is evaporated during the flight of the solution towards the collector due to the high voltage application \(^{87}\), no high temperature applied \(^{86}\). This is important for preserving the structure and achieving high encapsulation efficacy of the thermo-sensitive \(^{89}\) and volatile \(^{88}\) bioactive substances upon processing and storage \(^{46}\). Besides the advantage of low processing/production temperature, the electrospun nanofibers can also show an increase of the thermal stability \(^{89}\).\(^{90}\).\(^{91}\) during the subsequent thermal processing of the bioactive compounds, which are known to be highly sensitive to thermal treatments \(^{92}\) (polyphenols, principally anthocyanins) \(^{46}\). For example, volatile bioactive substances (carvacrol \(^{45}\)) encapsulated in the nanofibers have greater thermal stability than in the free form, which broadens the processing temperaturerange. Similar results were found in carvacrol and thymol loaded zein nanoparticles \(^{93}\); an enhanced thermal stability of EOs loaded-zein nanofibers was a consequence of the interaction \(^{94}\) between the polymer and EOs, which leads to a higher heat resistance of the resulting nanofibers, compared with the unprotected EOs. Electrosprayed hydroxypropylβ-cyclodextrin microcapsules containing maqui fruit extract were successfully obtained and had lower polyphenolic content reductions when exposed at high thermal conditions simulating baking conditions compared with the non-encapsulated samples \(^{46}\).

Chitosan/polycaprolactone electrospun nanofibers with chlorogenic acid loaded halloysite nanotubes (HNTs) had improved thermal stability due to the hydroxyl groups present in the cavity of HNTs interacting with bioactive molecules via hydrogen-bonds for efficient encapsulation and controlled release \(^{95}\).\(^{96}\). Immobilized enzymes present higher thermal stability than the free enzymes \(^{97}\).\(^{98}\), which makes the immobilization in crosslinked fibers to be effective in increasing thermal stability of enzymes which is beneficial for applications in which food products are subjected to high temperatures \(^{45}\).\(^{99}\).

The higher surface to volume ratio and porous structures generated through electrospinning have a beneficial effect for the long-term application of antimicrobials in comparison with the film casting approach. The morphology of the obtained structures had a significant effect regarding the long-term release (sustained antimicrobial activity), indicating the efficiency of the encapsulation to protect the active compounds by slowing down their volatilization \(^{90}\). Enhanced interactions/compatibility between the bioactive compounds and the encapsulating materials can sustain the release of antimicrobial agents over longer time from the fiber mats. For example electrospun nonwovens containing 30% carvacrol encapsulated in starch sustained antimicrobial activity for at least 30 days against L. monocytogenes, Salmonella Typhimurium, E. coli and S. aureus. \(^{45}\) due to the interactions between starch and carvacrol (evidenced by FT-IR and the increased viscosity due to the carvacrol addition). Therefore, the starch nanofibers are auspicious materials to be used as a vehicle for carvacrol release in antimicrobial and antioxidant food packaging \(^{43}\).

5. Conclusions
Electrospun nanocomposites/(nano)fibers (respectively electrospinning/electrospraying) require less amounts of raw materials, but properties are enhanced due to nanometric dimensions, which makes them a cost-effective alternative to conventional polymers and methods of packaging like Modified Atmosphere Packaging (MAP). Presently, encapsulation of bioactive compounds by electrospinning/electrospraying procedures is applied mainly at laboratory scale but also at pilot scale and industrially, with an impressive
research interest with the aim of application in various domains as biomedical, biosensors, food preservation and safety, etc. Although synthetic bioactive compounds are approved in many countries or food applications, they are not easily accepted by consumers, existing an increasing interest to replace them by natural bioactive compounds. The natural bioactive compounds can be used as food additives to preserve the food quality and safety, and as food supplements or nutraceuticals to correct nutritional deficiencies, maintain a suitable intake of nutrients, or to support physiological functions, etc. Bioactive compounds can be used as a single added component in a matrix or as blends of nanocomposites containing organic and inorganic bioactive compounds.

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Keywords

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