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Biopolymer-based nanoparticles and microparticles: Fabrication, characterization, and application

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ABSTRACT

Tailor-made microparticles and nanoparticles are finding increasing use in food products to alter their nutritional characteristics, flavor profile, appearance, rheology, stability, and processability. These particles are often fabricated from food-grade biopolymers, such as proteins and polysaccharides. Food biopolymers display a diverse range of molecular and physicochemical properties (e.g. molecular weight, charge, branching, flexibility, polarity, and solubility) which enables the assembly of colloidal particles that exhibit a broad range of functional attributes. By careful selection of appropriate biopolymers and assembly methods, biopolymer particles can be fabricated with tailored behaviors or features. In this article, we review recent developments in the design and fabrication of functional biopolymer nanoparticles and microparticles, and highlight some of the challenges that will be the focus of future research.

1. Introduction

Microparticles and nanoparticles are finding increasing application as ingredients in the food industry due to their particular physicochemical properties and functional attributes. The design of particles with specific properties has recently been driven by the application of nanotechnology principles to foods. Nanotechnology has been used to engineer particle-based systems for a variety of purposes in foods: encapsulation and release of active ingredients [1]; mimicking fat droplet functionality [2]; boosting salt perception; modifying rheology [3] and altering optical properties [4].

Microparticles were the main focus of research and development efforts in the 1980s, whereas nanoparticles have been the focus of more recent efforts [5]. The critical dimension that distinguishes microparticles from nanoparticles is still under debate. Some authors [6,7] have proposed a diameter of 100 nm as the upper size limit for nanoparticles as they claim that the properties of larger particles closely match those of bulk materials. However, this is highly dependent on material type and is not universally applicable. In general, nano- and microparticles display specific characteristics that differ from those of the corresponding bulk material. In addition, there is usually a gradual change in physicochemical properties and functional performance as the particle size changes, rather than a dramatic cut off at some particular dimension. Consequently, it is important to select a particle size that is most appropriate for a specific application, rather than deciding to use a nanoparticle over a microparticle, or vice versa.

Food-grade nanoparticles and microparticles can be fabricated from a range of different ingredients, including biopolymers, lipids, surfactants, and minerals. In this article, we focus on the utilization of biopolymers as the primary building blocks for nanoparticles and microparticles. Biopolymer particles are often classified according to their structures, such as (filled) hydrogel particles, inclusion complexes, and polyelectrolyte complexes (Fig. 1, Table 1). The dimensions of a biopolymer particle alter its functional performance in foods. For example, particle size influences the bulk physicochemical properties of foods (optics, rheology, and stability), encapsulation characteristics (e.g., loading, retention, and release), and behavior within the gastrointestinal tract (GIT; e.g., transport, degradation, interactions, and penetration). Furthermore, the high surface/volume ratio increases the importance of surface molecules over bulk molecules, which may impact phenomena that occur at interfaces, such as oxidation [8] or digestion [9].

In this review, we discuss the most prominent biopolymers and fabrication methods used to construct food-grade nanoparticles and

Abbreviations: DE, degree of esterification; GIT, gastrointestinal tract; SPI, soy protein isolate.

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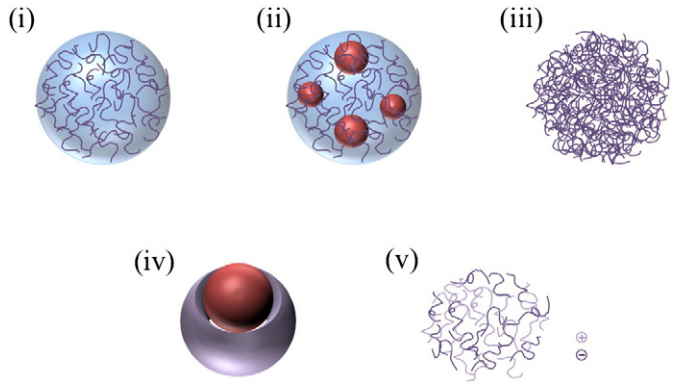

Fig. 1. Biopolymeric particles can adopt various forms. The most common forms are (i) hydrogel particles, (ii) filled hydrogel particles, (iii) biopolymeric particles, (iv) inclusion complexes and (v) polyelectrolyte complexes.

microparticles, highlight some of their most important recent applications, and outline future trends and challenges.

2. Particle fabrication techniques

One of the major areas of current research is the identification of appropriate building blocks and fabrication methods for creating food-grade biopolymer particles. Biopolymer particles can be prepared using many types of generally recognized as safe (GRAS) proteins and polysaccharides, which enable systems with different functional attributes to be created. This section provides an overview of recent research in identifying appropriate building blocks and fabrication methods for food-grade biopolymer particles.

2.1. Materials

The selection of a biopolymer or combination of biopolymers depends on several factors: the desired physicochemical and functional properties of the particles (e.g., size, charge, polarity, loading capacity, permeability, degradability, and release profile), the properties of the biopolymers (e.g., charge, polarity, and solubility), and the nature of any enclosed active ingredient (e.g. charge, polarity, solubility, and stability).

2.1.1. Proteins

Proteins can be used in their natural state, or they can be chemically, physically, or enzymatically modified to modulate their functional attributes [10,11]. Consequently, it is often possible to fine-tune the functional performance of proteins for specific applications. Most proteins are easily digested within the human GIT, which is important for ensuring the eventual release of bioactive components after ingestion [12–14]. Furthermore, proteins often display anti-oxidant properties, which may be useful to protect chemically labile active ingredients [8]. After particle fabrication, a chemical, physical, or enzymatic hardening step can be used to cross-link proteins and stabilize particle structures [15]. Protein particles are often highly sensitive to alterations in pH, ionic strength, and/or temperature because these trigger changes in their surface charge and hydrophobicity. Proteins used to produce biopolymer particles can be divided into animal- and plant-derived proteins.

2.1.1.1. Animal-derived proteins. Albumins are water-soluble globular animal proteins that are only moderately soluble in salt solutions and denature upon heat treatment. Albumins are attractive proteins to produce biopolymer particles as they are widely available in a pure form, are biodegradable, and non-toxic. They contain reactive groups (carboxylic acid, thiol and amino groups) that allow the attachment of active components to the particle surface or, prior to particle production, to the particle interior, in a relatively simple way [11].

Caseins are proteins isolated from milk, in which they naturally occur in micelles. They can be used to form gel-like structures by addition of acids, calcium, or enzymes, or they can be used to build structures with other biopolymers based on their charge and hydrophobic characteristics. Caseins have been used to encapsulate various kinds of bioactive agents in molecular complexes, micelles, and hydrogel particles [16–18].

Gelatin is a water-soluble protein that is relatively cheap and displays interesting functional properties useful for constructing biopolymer particles. It is available in both low and high isoelectric point forms that make it particularly suitable for constructing biopolymer particles based on electrostatic interactions. It forms gels upon cooling with properties that depend on protein concentration, pH, cooling rate, and holding temperature [3]. However, glutaraldehyde cross-linking is often required to give gelatin particles enough stability against swelling/dissolution upon heating. The cross-linking density determines particle stability as well as the release profile of encapsulated compounds. Biopolymer particles containing albumin and gelatin have recently been produced by liquid antisolvent precipitation [19,20] or coacervation [21].

Fibroin has been used widely in biomedical applications, because of its biocompatibility, biodegradability, anti-microbial properties, and thermal stability. Subia and Kundu [22] successfully used it in combination with albumin to fabricate biopolymer particles with an average diameter of 200 nm.

Whey protein is one of the most commonly used food ingredients for forming biopolymer particles. It can be gelled by heat-set gelation (heating above the thermal denaturation temperature under appropriate pH and ionic strength conditions) or by cold-set gelation [23]. Biopolymer particles have recently been produced by controlled thermal denaturation using various whey proteins, such as β-lactoglobulin [24,25] and lactoferrin [26]. Antisolvent precipitation methods have also been used to produce whey protein particles [27]. Cold-set gelation

Table 1
Definition of words and phrases used in the review.

Word/acronym	Definition
Biopolymeric particles	(Cross-linked) particles composed of polymers with a dense matrix which only incorporate a limited amount of liquid
Coacervation	Separation of two liquids into two phases which contain a different concentration of the components
Extrusion	The act of forcing a biopolymer solution through a nozzle into a gelling environment
Filled hydrogel particles	Particles which contain one or more smaller particles (e.g., fat droplets, fat crystals or biopolymeric particles) trapped in larger hydrogel particles
Gelation	The transformation of a liquid into a semi-solid or solid
Hydrogel particles	Soft cross-linked particles composed of gelled polymers which incorporate appreciable amounts of liquid/solvent into the polymer network structure
Inclusion complexes	Molecular encapsulation forms in which (bio-)active guest molecule(s) are trapped within cavities of the host molecule
Liquid antisolvent precipitation	A particle production method based on the reduction of solvent power of a biopolymer solution
Polyelectrolyte complexes	Complexes formed through simple electrostatic attraction between oppositely charged biopolymers
Polysaccharide	Macromolecules composed of monosaccharides linked through glycosidic bonds
Protein	Macromolecules composed of amino acids linked through peptide bonds
Zeta potential	Measure of the effective electric potential difference of a charged colloid, which depends on the surface charge density and the presence of any strongly bound counter-ions