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Protein–polysaccharide associative interactions in the design of tailor-made colloidal particles

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ABSTRACT

This article reviews some recent advances in the use of diverse protein–polysaccharide associative interactions in the design of colloidal particles having potential to be used for both fortification of food colloids with health-promoting bioactive compounds with better control of their physical stability and breakdown within the gastrointestinal tract. Protein–polysaccharide associative interactions are discussed in the following aspects: (i) the formation of micro- and nanoparticles for the delivery of health promoting ingredients (nutraceuticals); (ii) the controlled gastrointestinal fate of colloidal particles; (iii) the formation of biopolymer-based particles as fat replacers; and (iv) the behavior of colloidal particles as stabilizers of emulsions and foams. The first aspect concerns soluble protein–polysaccharide complex particles (electrostatic nanocomplexes, complex coacervates, covalent conjugates), mixed hydrogel particles, and nanoemulsion-based delivery systems.

1. Introduction

Associative interactions between two main classes of food biopolymers, namely, proteins and polysaccharides, which are Generally Recognized as Safe (GRAS), are the primary basis of well-known and efficient methods (complexation and gel formation in a continuous phase and at interfaces) traditionally used for improving the physical stability and textural characteristics of a wide range of food colloids (dispersions, emulsions, foams, gels and their mixed variants) in food manufacture [1•,2•,3••,4•]. A distinguishing feature of these interactions is their great diversity. They include both (i) non-covalent attractive forces (physical: electrostatic - between opposite charges, hydrogen bonding, hydrophobic, van der Waals), (ii) covalent (chemical) bonding, which are determined by the wide variety of functional groups (ionic, polar, non-polar), as well as (iii) the conformations (globule, random coil, rigid rod, helix, etc.), sizes and molar weights of the interacting biopolymers [1•,3••,5••,6••].

Within recent years there has been a growing research interest in the potentialities of using of the associative interactions between food proteins and polysaccharide from natural sources in designing of tailor-made colloidal structures that, on the one hand, might be used in the manufacture of foods with enhanced nutritional quality and health benefits [3••,7••,8,9••,10••] and, on the other hand, could respond additionally to increased customer requirement for 'clean' labels on food and beverage products [3••,9••].

This review focuses on recently achieved insights into the contribution of the protein – polysaccharide associative interactions on: (i) the formation of micro- and nanoparticles for delivery of health promoting ingredients (nutraceuticals); (ii) the control of the gastrointestinal fate of colloidal particles; (iii) the formation of fat-replacers; and (iv) the behavior of colloidal particles as emulsifying/foaming agents. To meet the demand of novelty, references to publications that have mainly appeared in the past 2–3 years have been covered.

2. Formation of micro- and nanoparticles for the delivery of health promoting ingredients

The health promoting ingredients, or so-called nutraceuticals, have both a nutritional and a medically proven prophylactic value [1•,9••,11,12]. For example, the wide and diverse class of nutraceuticals includes such bioactive substances as ϖ-3 and ϖ-6 fatty acids, phospholipids, non-enzymatic antioxidants (vitamins, carotenoids, polyphenols, minerals etc.), antioxidant co-factors, vitamins, vitamin-like substances, etc. [1•]. Most of these require the protection against both oxidation and degradation during food processing and storage (pH, high temperature, daylight, metal ions) as well as their controlled release within a particular region of the gastrointestinal tract (GIT) [7••,10••,13•,14••].

Due to the lipophilic nature of the most nutraceuticals, designing ways of their incorporation into non-fat aqueous foods and beverages have attracted special interest [1•,4•,13•]. By now, it has been well established that biopolymer-based delivery systems, owing to the generally amphiphilic nature of the biopolymer molecules and their

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aggregates, can provide a combination of different intermolecular forces for the effective retention of both hydrophobic and hydrophilic nutraceuticals [1*,8,10**,13*,14**,15*,16*,17*,18**,19*]. Additionally, the biopolymers themselves can show a beneficial biological activity as, for example, the biopharmaceutical properties (such as muco-adhesiveness and ability to open the epithelial tight junctions) of chitosan [20], the antioxidant activity of β-lactoglobulin (BLG) owing to its free thiol groups [21] or the high affinity of pullulan towards the liver that has potential applications in drug delivery systems [22].

In estimating the suitability of biopolymer-based particles as delivery systems for a specific bioactive, the loading capacity, both the encapsulation and retention efficiencies, are typically the factors of most interest [23**]. The physical stability of delivery systems can also often be improved by biopolymer crosslinking (enzymatic, physical or chemical) or a biopolymer coating [10**,24**].

Biopolymer-based delivery systems may be divided into two main groups depending on their size, namely - nanoparticles - when at least one of particle dimensions is smaller than 100 nm, and - microparticles - when one of particle dimensions is smaller than 1000 μm [10**,23**,14**,25**,26*]. It is vital to note that nanoparticles have several clear advantages over microparticles due to their higher surface area/volume ratio, providing the increased load solubility, the high dispersion of dose, the enhanced bioavailability of the cargo molecules, plus improvement of targeting and controlled release [14**,27].

Protein–polysaccharide associative interactions have a profound impact on determining the structure, the physical stability and the functionality of such delivery systems that will be described in the following sections.

2.1. Soluble protein–polysaccharide complex particles

2.1.1. Electrostatic nanocomplexes

Electrostatic nanocomplexes are formed due to the attractive electrostatic interactions between the oppositely charged molecules/aggregates of proteins and polysaccharides. Because of this, pH and ionic strength play an extremely important role in determining their structure and properties [10**].

Soluble protein–polysaccharide electrostatic nanocomplexes have been used recently as:

(i) nanocapsules for hydrophobic bioactive molecules [13*,28,29].
(ii) mixed emulsifying/foaming stabilizers in a single stage of homogenization [5**,13*].

Protein–polysaccharide electrostatic complexation during [30] or after [31] the particle formation can improve the stability not only for nutraceuticals encapsulated in the complexes but also for the protein itself composing the particles, by increasing the steric and electrostatic repulsions between the complex particles compared to the protein alone [10**, 13*]. Both hydrophobic (curcumin, β-carotene, vitamin D_2) and hydrophilic (folic acid) model nutraceuticals have been effectively stabilized by their encapsulation into the soluble electrostatic nanocomplexes of β-lactoglobulin (BLG) with sodium alginate (Na-Alg) formed in the pH range between the pK_a of the polysaccharide and the isoelectric point (pI) of the protein [13*]. Fig. 1 shows an example of this stabilization for curcumin.

Further developments have been made of the 'layering approach' as applied to nanoemulsion stability, based on protein–polysaccharide electrostatic associative interactions [9**,32]. Most commonly the protein forms the inner adsorbed layer and the polysaccharide - an outer layer. The latter gives the additional steric and electrostatic stabilization [5**,7**]. In addition, the protective complex adsorbed layer can change the overall particle density as well, and, hence, slow down creaming after the initial emulsion formation. In addition, the increase in the viscosity of the surrounding medium owing to the protein–polysaccharide associative interactions can also slow down this process [10**]. Fig. 2 illustrates an example of the use of the 'layering approach' for the emulsion stabilization.

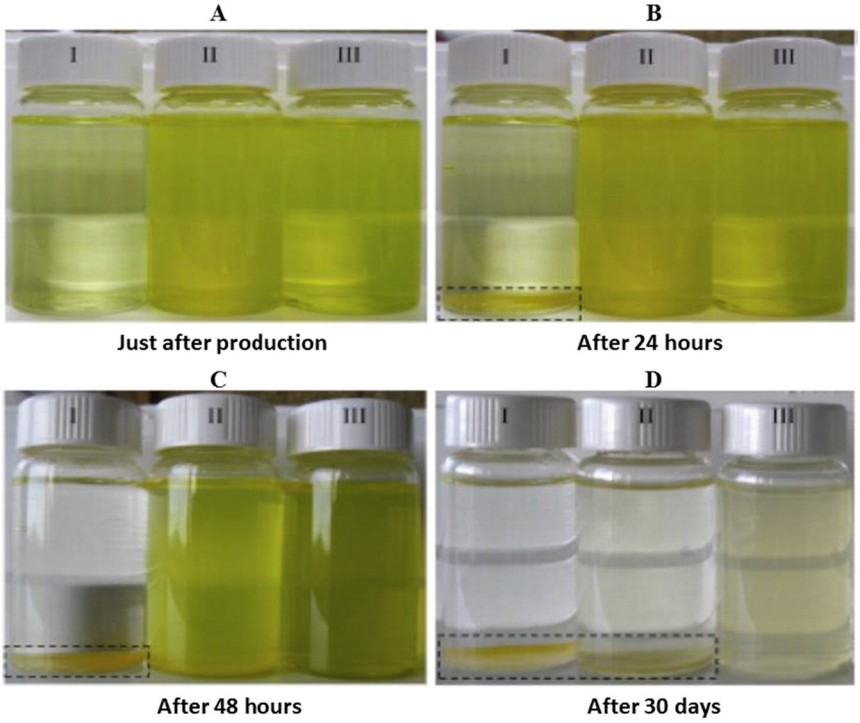

Fig. 1. Effects of curcumin nanoencapsulation on its colloidal stability at pH 4.25 (I: dissolved curcumin in ethanol added to deionized water; II: dissolved curcumin in ethanol added to a BLG dispersion (0.1% *w*/w); III: dissolved curcumin in ethanol added to BLG-Na-ALG soluble complexes (Na-ALG/BLG weight ratio of 0.75).
(Reproduced with permission from [13*].)