Trends in Food Science & Technology 68 (2017) 56–69

Contents lists available at ScienceDirect

Trends in Food Science & Technology

journal homepage: http://www.journals.elsevier.com/trends-in-food-science-and-technology

Review

Functional colloids from proteins and polysaccharides for food applications

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ARTICLE INFO

Article history:
Received 16 March 2017
Received in revised form
15 August 2017
Accepted 15 August 2017
Available online 18 August 2017

Keywords:
Complex particles
Dry-heat conjugates
Pickering stabilization
Emulsions
Hydrogels
Oleogels
Food formulations

ABSTRACT

Background: Developing novel food structures is nowadays becoming an attractive technology for food product innovation because they can be used to control textural properties, oral processing and perception, as well as biofunctionality in the human body. Proteins and polysaccharides are among the most abundant natural raw materials that can be used for creating novel food structures owing to their supramolecular interactions driven by attractive or repulsive forces. These two classes of biopolymers can be used to create different types of colloidal systems with unique properties, such as nano- or microparticles, hydrogels, films, emulsions, oil-filled hydrogels, foams, and oleogels, to name a few.

Scope and approach: In this review, we discuss a range of functional colloids which can be fabricated by exploiting spontaneous interactions of proteins and polysaccharides. Besides, the fundamental theories of proteins and polysaccharides interactions that can affect the structural formation are described. Furthermore, potential food applications of some selective functional colloids are also discussed with illustrative examples.

Key findings and conclusions: The synergistic interactions of proteins and polysaccharides in their mixed system and a more complex system where a hydrophobic phase is present, could be employed to obtain various colloidal structures with numerous promising applications in the food industry.

1. Introduction

In the current scenario, manipulation of the macroscopic properties of food products such as shape, texture, consistency and flavor is popularly identified through molecular gastronomy terminology, but from a scientific point-of-view, it can be considered as an extension of soft matter physics (Van der Sman & Van der Goot, 2009). The latter has received a lot of attention, as indicated by the growing number of food-related papers published in multidisciplinary journals in the recent years. Contrary to other soft matter systems, a strong emphasis is focused on the taste and flavor properties when dealing with edible soft matter systems (Mezzenga, 2007; Van der Sman & Van der Goot, 2009). Interestingly, foods are perceived by their texture, and the textural properties are known to strongly modulate the taste (De Lavergne, van Delft, van de Velde, van Boekel, & Stieger, 2015). Therefore, in food systems, the formation of functional food colloids through understanding of the interactions of food ingredients is an interesting challenge to be pursued not only by researchers but also by food manufacturers.

Structuring foods are mainly done by a complex assembly of various food materials such as proteins, polysaccharides, lipids, sugars, emulsifiers, minerals, water and other minor components. Among these components, proteins and polysaccharides are the most utilized materials in food processing. They play a synergistic role in structuring the bulk phases of colloid systems, while also providing interface-stabilizing properties through a combination of various molecular interactions with/in the dispersed phases. These molecular interactions establish the mesoscopic structures as fundamental building blocks, such as colloidal particles (Jones, Decker, & McClements, 2010), gas bubbles (Dickinson, 2010), emulsion droplets (Jones, Decker et al., 2010), or gel networks (Le, Rioux, & Turgeon, 2017). The length scale of these mesoscopic structures is in the order of microns. These microstructures

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http://dx.doi.org/10.1016/j.tifs.2017.08.003
0924-2244/

influence the bulk properties of food, for instance, rheology (i.e., the mechanical and flow properties of the dispersion) or other textural properties. These features have been of great scientific and industrial interest in the past two decades as indicated by some notable world-wide institutions that consistently work on this area of protein and polysaccharide interactions (Table 1).

In this review paper, the fundamental insights of protein-polysaccharide interactions are firstly discussed with respect to the important factors that can affect the interactions. Next, we emphasize the recent research of functional colloid formation based on protein-polysaccharide interactions. Here, some interesting colloid structures such as micro/nanoparticles, hydrogels, films, simple and multiple emulsions, oil-filled hydrogel particles, foams, and oleogels are discussed. Following the functional colloid formation, we discuss current and future potential applications of these colloids in foods.

2. Protein-polysaccharide interactions

In this section, the fundamental principles of protein-polysaccharide interpolymeric interactions are discussed. Generally, interactions between proteins and polysaccharides may occur non-covalently and covalently (Dickinson, 2008). Non-covalent interactions are non-specific and can be divided into two groups: attraction and repulsion between unlike biopolymers. These two types of polyelectrolyte interactions in solution contribute to complex formation and the immiscibility (thermodynamic incompatibility) of biopolymers. These interactions are mainly affected by internal factors (i.e. pH, ionic strength, conformation, charge density and concentration) and external factors (i.e. physical factors such as temperature). Covalent interactions are highly specific, establishing permanent binding and irreversible interaction between proteins and polysaccharides (Schmitt, Sanchez, Desobry-Banon, & Hardy, 1998). Both non-specific and specific interactions have their own functionality which is affected by the magnitude of these interactions (attractive or repulsive, weak or strong).

2.1. Non-covalent interactions

Proteins and polysaccharides may interact non-covalently which may occur between charged groups (electrostatic), hydrogen and hydrophobic groups. These interactions are generally weaker than covalent interactions (Schmitt et al., 1998). Electrostatic interactions play dominant role in the interactions of proteins and polysaccharides. They can be repulsive or attractive which mainly depends on the electrical charge of the proteins and the polysaccharides. Attractive electrostatic interactions occur if oppositely charged proteins and polysaccharides meet together in the mixed biopolymer system. This interaction may be weak or strong leading to the formation of soluble or insoluble complexes, respectively. Soluble complexes are formed by binding of anionic polysaccharides to some cationic reactive sites of proteins (at pH close to the isoelectic point (pI) of the protein), which causes the colloidal complexes to be relatively stable because the number of opposite charges carried by the two macro-ions is not equal. The resulting net charge allows the complex solubilization by interaction with solvent molecules. However, when the number of opposite charges carried by both biopolymers is equal, the resulting complex charge is zero and the complexes become insoluble leading to a phase separation between the complexes and solvent (Turgeon, Beaulieu, Schmitt, & Sanchez, 2003) (Fig. 1). Furthermore, several physicochemical factors influence the overall and local charge of the protein and polysaccharide complexes. The most critical factors are mainly composed by pH, ionic strength, protein to polysaccharide ratio and concentration. Some other factors such as the biopolymer molecular weight and flexibility, the charge density, and the physical forces have been shown to also influence complex formation. However, the ratio and concentration of biopolymers, and pH play the important role towards the solubility of protein-polysaccharide aggregates (Turgeon, Schmitt, & Sanchez, 2007).

Repulsive electrostatic interactions occur where two strongly (but oppositely) charged biopolymers are mixed together at very low ionic strength. Depending on the concentration of biopolymers in the mixture, they may exist in a single phase system (where two separate entities distribute uniformly throughout the medium) or a segregative phase (two distinct phases with each phase comprising a different biopolymer) (Fig. 1). In this case, at low concentration, two biopolymers can be co-soluble in a single phase, whereas at high concentration, phase separation (segregation) between the two biopolymers occurs (Patino & Pilosof, 2011). Phase separation

Table 1
Principal investigator/institution with research focus on protein-polysaccharide interactions in mixtures or complex systems.

Protein-polysaccharide-based functional colloids	Institution	Principal Investigator
O/W emulsions, heat-treated microparticles, glycated conjugates	School of Food Science and Nutrition, University of Leeds, UK	Eric Dickinson
Complex coacervation, phase separation of mixed biopolymers, emulsions	Materials and Analytical Science, Glyndwr University, Wrexham, UK	Peter A. Williams
Electrostatic complexes, phase separation of mixed biopolymers, emulsions	Phillips Hydrocolloid Research Centre, Cardiff, UK	Glyn O. Phillips
O/W emulsions, heat-treated microparticles, glycated conjugates	Department of Food Science, University of Massachusetts Amherst, USA	David Julian McClements
Microgel particles, O/W emulsions	Department of Food Science, Purdue University West Lafayette, USA	Owen Griffith Jones
Biopolymers mixed gels	Department of Food, Bioprocessing and Nutrition Sciences, NCSU, USA	Edward Allen Foegeding
Complexes coacervates	Department of Food Science, Rutgers Unversity, USA	Qingrong Huang
Polyelectrolyte complexes	Department of Nutritional Science, University of Connecticut, USA	Yangchao Luo
Electrostatic hydrogel, complexes coacervates	Institut sur la nutrition et les aliments fonctionnels- INAF, Université Laval, CA	Sylvie Turgeon
Emulsion-templated oleogels, concentrated emulsions, hydogels	Previously at Faculty of Bioscience Engineering, UGent, BE	Ashok R. Patel
Electrostatic nanocomplexes, O/W emulsions, glycated conjugates	Particle and Interfacial Technology, UGent, BE	Paul Van der Meeren
Complexes coacervates	Physical Chemistry and Soft Matter, Wageningen University, NL	Renko de Vries
Complexes coacervates	Debye Institute for Nanomaterials Science (DINS), University Utrecht, NL	C.G. (Kees) de Kruif
Heat-treated microparticles	Food Physics and Meat Science, University of Hohenheim, DE	Jochen Weiss
Double emulsions, complexes coacervates	Departamento de Preparatoria Agricola, Universidad Autónoma Chapingo, Mexico	Consuelo Lobato-Calleros
Electrostatic complexes, glycated conjugates	Phillips Hydrophilic Colloid Research Center, Hubei University of Technology, CN	Katsuyoshi Nishinari