Advances in Colloid and Interface Science 239 (2017) 127–135

Contents lists available at ScienceDirect

Advances in Colloid and Interface Science

journal homepage: www.elsevier.com/locate/cis

Formation and functional properties of protein–polysaccharide electrostatic hydrogels in comparison to protein or polysaccharide hydrogels

Xuan T. Le, Laurie-Eve Rioux, Sylvie L. Turgeon *

STELA Dairy Research Centre, Institute of Nutrition and Functional Foods, Faculty of Agriculture and Food Science, Université Laval, 2425 rue de l'agriculture, G1V 0A6, Québec, Canada

ARTICLE INFO

Available online 3 May 2016

Keywords:
Protein
Polysaccharide
Mixed electrostatic gel
Gelation water holding properties
Functional properties

ABSTRACT

Protein and polysaccharide mixed systems have been actively studied for at least 50 years as they can be assembled into functional particles or gels. This article reviews the properties of electrostatic gels, a recently discovered particular case of associative protein–polysaccharide mixtures formed through associative electrostatic interaction under appropriate solution conditions (coupled gel). This review highlights the factors influencing gel formation such as protein–polysaccharide ratio, biopolymer structural characteristics, final pH, ionic strength and total solid concentration. For the first time, the functional properties of protein–polysaccharide coupled gels are presented and discussed in relationship to individual protein and polysaccharide hydrogels. One of their outstanding characteristics is their gel water retention. Up to 600 g of water per g of biopolymer may be retained in the electrostatic gel network compared to a protein gel (3–9 g of water per g of protein). Potential applications of the gels are proposed to enable the food and non-food industries to develop new functional products with desirable attributes or new interesting materials to incorporate bioactive molecules.

Contents

* Corresponding author at: Postal address: STELA, Université Laval, Pavillon Paul-Comtois, 2425 rue de l'agriculture, Québec G1V 0A6, Canada. Tel.: +1 418 656 2131x4970; fax: +1 418 656 3353.
E-mail address: Sylvie.Turgeon@fsaa.ulaval.ca (S.L. Turgeon).

http://dx.doi.org/10.1016/j.cis.2016.04.006
0001-8686/

1. Introduction

Proteins and polysaccharides are classified as biopolymers due to their natural origins and their large polymeric structures. They are commonly used as ingredients in food products for their important roles in the structure and stability of processed foods such as thickening, stabilizing, gelling and emulsifying agents, etc. Their simultaneous addition may induce intermolecular interactions offering ways to diversify their functionality. The control of these macromolecular interactions is therefore of high interest for the development of novel food products. For example, proteins and polysaccharides can be processed into functional ingredients to form edible films, to encapsulate vitamins and flavors, to replace fat materials and to form novel semi-solid food products as electrostatic gels [1–4].

When proteins and polysaccharides are mixed together in water, depending on environmental conditions such as pH and ionic strength, two different types of interactions can occur: thermodynamic incompatibility also known as segregative phase separation or thermodynamic compatibility resulting in an associative phase separation. Segregative conditions prevail when there is no associative interaction for example between a protein and a neutral polysaccharide or with a polysaccharide wearing charges similar to the protein (as anionic polysaccharide with pH > isoelectric point (Ip) of the protein). More detailed information on protein–polysaccharide segregative systems and their functional properties are discussed in several reviews [5–8]. On the other hand, thermodynamic compatibility is usually induced by associative electrostatic interactions between proteins and polysaccharides when both biopolymers carry net opposite electric charges. These interactions occur at a pH between the proteins' Ip and the polysaccharides' pK_a. Under those conditions, different types of structure can be formed including coacervates, complexes and gels depending on preparation conditions. These structures may be modulated by several factors such as the biopolymers molecular conformation, the charge density and the protein–polysaccharide binding affinity [4]. Coacervates are the result of a phase separation into two liquid phases. The coacervate is found in the phase in which the biopolymers are concentrated while the other phase contains mainly the solvent [9,10]. Interacting protein and polysaccharide may also form complexes which are aggregates of fractal nature and separate in a phase denser than coacervates. The aggregates' properties depend on the protein–polysaccharide ratio. When the protein to polysaccharide ratio allows to reach neutrality of the biopolymer system, a maximum yield of insoluble complex is produced. Soluble complexes may be obtained when the ratio is far from equivalent due to the repulsion between residual charges on the biopolymers [4]. For the interested reader, several reviews on protein–polysaccharide coacervates and complexes detailing the parameters influencing their formation and their functional properties for food applications are available [4,9,11–15].

Associative interactions in mixed protein–polysaccharide systems and formation of complexes and coacervates were studied since the nineteen thirties [16]. Ten years ago, the formation of gel under electrostatic associative conditions was first reported for a protein–polysaccharide mixed system [17]. Interaction under quiescent conditions made possible to obtain a gel with a very low solid content (0.03%) without any heat treatment [18]. It was suggested that they may be classified as hydrogel as for each g of biopolymers up to several hundred g of water were retained [19]. Hydrogels are three-dimensional polymeric networks formed by crosslinking polymer chains through physical, ionic or covalent interactions, that can absorb a large amount of water while maintaining their structural integrity [20,21]. However, the amount of water to be considered as large has not been clearly defined and several authors are using the term hydrogels for any gelled structure containing water which may induce confusion in the interpretation. According to Gulrez and collaborators [22], the terms gels and hydrogels have been used interchangeably by food and biomaterial scientists, respectively.

In this paper, protein based and polysaccharide based gels will be briefly introduced and their gelling conditions will be presented for the purpose of comparison with protein–polysaccharide associative mixed gels. Then, recent progress on the formation and functional properties of protein–polysaccharide electrostatic gels with a particular focus on the effects of the structural characteristics of biopolymers and some environmental factors will be reviewed. Other gelling systems such as synthetic polymer gels are outside the scope of this publication and interested readers are invited to consult other reviews for these types of gelling systems [23,24].

2. Hydrogels based on protein, polysaccharide and protein–polysaccharide mixtures

2.1. Protein hydrogels

Protein gelation is an important phenomenon to obtain desirable sensory and textural attributes of foods. The gelation of protein has been traditionally achieved by physical treatment (heating, high pressure), enzymatic and chemical treatments (acidification and addition of salt). Most of these gelation methods rely on a mechanism involving unfolding of the native protein structure and aggregation into a gel network that can hold water within its structure. The main protein gelation methods were reviewed by Totosaus et al. [25]. Generally, the protein network is stabilized through non-covalent cross-links such as hydrophobic/electrostatic interactions, hydrogen bonds and/or covalent bonds such as disulfide bonds. The minimal protein concentration needed to form a gel is specific to each protein and it is influenced by their structural characteristics and the gelling conditions (Table 1). Some examples of minimal concentration values are 0.6% for gelatin [26], 3% for egg albumin [26], 6.6% for soy proteins [27] and from 4–12% for whey proteins depending on pH and ionic strength [28].

The functional properties of protein hydrogels (gel strength, elasticity, water holding capacity, etc.) depend on the protein intrinsic characteristics, the protein concentration, the ion type and concentration, the pH as well as the processing conditions used to induce gelation (temperature, time, rate of heating, high pressure treatment, etc.). Globular protein gels have been categorized in fine stranded and particulate gels [29,30]. The former is a transparent fine-stranded protein hydrogel formed when protein solutions are heated at pH far from protein's Ip with low ionic strength. The latter is obtained at pH close to protein's Ip and/or at high ionic strength, particulate protein hydrogels are then formed. This behavior has been reported for whey proteins [29–31], egg proteins [32] and other globular proteins [33]. The particulate hydrogels are coarser, opaque, weak and brittle and retain less water in their structure after centrifugation compared to a fine stranded protein gel [34,35]. Additional information on protein hydrogels properties are presented in Section 6. More details on formation, structure and applications of protein gels can be found in several publications [36–40].

2.2. Polysaccharide hydrogels

Polysaccharide with their molecular weight ranging from several hundred thousand Daltons to millions of Daltons through various intermolecular interactions allow gel formation at concentrations lower than 1% [41] lower values than the one required for protein gelation (Table 1). Several factors influence polysaccharides gelation. Molecular characteristics as the molecular weight, the monosaccharide composition, the charge density (sulfate/carboxylic groups) and the conformation (flexibility) are known important factors. Extrinsic factors as the temperature, the presence of specific counter ions and/or the pH also modulate polysaccharide gelation. Variation in some of these extrinsic factors may provoke changes in the polysaccharide conformation from a disordered to an ordered state [42]. Intermolecular associations between ordered domains form physical crosslinks of the network entrapping water. The driving force for cross-linking varies between