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Review

Fabrication methods of biopolymeric microgels and microgel-based hydrogels

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ABSTRACT

Biopolymeric microgels made of proteins and/or polysaccharides provide a renewable source for enteral nutrition, interface stabilization, controlled release applications and etc. These microgels consist of physically, chemically, or enzymatically cross-linked biopolymer molecules that trap and hold water within the particle network. They can be formed from single or mixed biopolymers using a variety of methods based on molecular association mechanisms and mechanical processes. Biopolymer type and microgelation method determine the main properties of resulting microgels. Certain challenges associated with the small dimensions of microgels can be addressed through the development of immobilized microgel matrices, in which individual microgel particles are entrapped inside a hydrogel or cross-linked to form a macroscopic network. Immobilized microgel matrices can provide unique properties and additional applications relative to bulk hydrogels or individual microgels alone. This article reviews manufacturing methods for producing biopolymeric microgels, and describes formation of microgel-based hydrogels via effective immobilization of microgels within a network.

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1. Introduction

A microgel particle is defined as a microscopic three-dimensional network comprising cross-linked polymer molecules dispersed in a proper solvent (Funke, Okay, & Joos-Muller, 1998; Shewan & Stokes, 2013). The stable structure of microgels owes to the presence of covalent bonds and strong noncovalent interactions (Pelton & Hoare, 2011). In general, colloidal microgels can be categorized into two subclasses: the nanogels, and the microgels which have diameters <0.5 μm and 0.5–5 μm, respectively (Vinogradov, 2010). Most microgel particles have high water absorption tendency due to the hydrophilicity of constituting polymer chains; however, the particles undergo swelling rather than being dissolved in an aqueous phase. This behavior is mainly a consequence of the cross-linked nature of the microgel structure (Hamidi, Azadi, & Rafiei, 2008). Microgels show reversible swelling and deswelling characteristics in response to external stimuli, such as alterations in temperature, pH value, ionic strength, and solvent composition. This allows designing engineered particles with controllable and environment-responsive properties via modulating inter-polymer and polymer–water interactions (Pich & Richtering, 2010 (Chapter 1); Sierra-Martin, Lietor-Santos, Fernandez-Barbero, Nguyen, & Fernandez-Nieves, 2011).

Various sophisticated morphologies, including core-shell particles, Janus microspheres, interpenetrating polymer networks, microgels enclosing nanoparticles, and functionalized microgels can be fabricated for diverse purposes such as cargo delivery and sensing. Biodegradability and biocompatibility are important issues for employment of microgels in many applications for example biomedical, tissue engineering, and food structuring (Oh, Lee, & Park, 2009; Pelton & Hoare, 2011). In general, biodegradable polymers that are most commonly used as the main building blocks of biodegradable microgels can be classified into three categories: 1) naturally occurring biopolymers including plant and animal carbohydrates (such as alginate, starch, cellulose, carrageenan and chitosan) and proteins (such as gluten, soy protein, corn zein, casein, whey protein, gelatin, and collagen), 2) synthetic biopolymers including polylactide, polycaprolactone and poly(vinyl alcohol); and 3) microbial polyesters such as poly(hydroxyalkanoate)s (Hanna & Xu, 2009; Niaounakis, 2013 (Chapter 2); Rhim, 2013). Among these options, renewable biopolymers from agricultural resources are gaining increasing attention due to being inexpensive, readily available, significantly biocompatible and totally biodegradable (Hanna & Xu, 2009).

Microgel particles based on natural biopolymers are fabricated through different physicochemical and mechanical approaches, for example, molecular association, atomization and emulsion-based processes. Microgel preparation method and formation conditions such as pH value, temperature, ionic strength, shear stress, solvent type, biopolymer concentration, and the nature of crosslinking agent and crosslinking degree determine the structure, electrical charge, and physicochemical properties of resulting microgels. Profound knowledge about biopolymer properties, possible interactions between biopolymers, structural assembly and hierarchy, as well as, gelation principles (Burey, Bhandari, Howes, & Gidley, 2008; Jones & McClements, 2010) are required to accomplish a successful and well controllable process that confers tailored characteristics to final microgel particles.

This communication provides a review about the fabrication methods of protein and polysaccharide-based microgels followed by describing microgel-based hydrogels preparation via immobilization of microgels within a network.

2. Fabrication methods

The techniques used to fabricate microgel particles can be categorized into molecular association-based procedures and mechanical practices. A great majority of the methods combine droplet/particle formation with gelation.

2.1. Molecular association

Biopolymers molecular association is the simplest way to form microgel particles (Vinogradov, 2010). It is carried out through assembling a single type of biopolymer (self-association) or alternatively mixed biopolymer types (associative complexation).

2.1.1. Self-association

Self-assembled microgels are formed from single biopolymer under appropriate prevailing condition where biopolymer–biopolymer interactions are preferable over biopolymer–solvent interactions (McClements, 2015, Chapter 7). Thermal denaturation, crosslinking, desolvation and simple coacervation are the routes that promote self-association (Jones & McClements, 2012).

2.1.1.1. Thermal denaturation of globular proteins. Heat-induced microgels can be formed by simply heating solutions of globular proteins (for example egg white proteins, soybean proteins and whey proteins) above their thermal denaturation temperature (McClements, 2015). Spherical aggregates tend to be formed at pH values close to the isoelectric point (pI) or at high ionic strengths, because of a weaker electrostatic repulsion between protein molecules (Nicolai, 2016). In this regard, whey protein microgels are formed by thermal treatment of the corresponding protein solution in slightly acidic pH values (pH 5.7–6.1) and at relatively low protein concentrations (~1–3 g L^{-1}) (Jones, 2014). The surface hydrophobicity of globular proteins increases upon their thermal denaturation, which affects the surface activity, binding capacity, and aggregation behavior of proteins. Consequently, proteins aggregate via hydrophobic interactions and intermolecular disulfide bonds. Initial biopolymer concentration, heating temperature, heating time, pH value, and ionic strength influence and control the size and charge of the microgels generated (Nicolai & Durand, 2013).

Microgels can also be fabricated through the cold-set gelation of pre-heated globular proteins. For this purpose, a protein solution is at first heated to unfold under conditions where filament formation is favored (pH values away from the pI and low ionic strengths). The solution conditions are then manipulated so that the protein filaments associate with each other, for example, by adjusting pH close to the pI or by adding calcium chloride at neutral pH (McClements, 2015). Soy protein isolate (SPI) microgels (28–179 nm) were successfully prepared by supplementing $CaCl_2$ into a diluted solution of SPI soluble aggregates (6 mg mL^{-1}). Calcium ions shielded the negative charges on SPI aggregates and formed bridges between neighboring protein chains (Zhang, Liang, Tian, Chen, & Subirade, 2012).

2.1.1.2. Crosslinking polysaccharides and random coil proteins. Microgel particles can be formed by crosslinking gelling biopolymers at a concentration below that required for formation of a macroscopic gel (McClements, 2015). Various crosslinking substances depending on biopolymer type are employed, among which use of chemical reagents (such as glutaraldehyde), enzymes (such as transglutaminase), and mineral counterions (such as cal-