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Functional hydrogel microspheres: Parameters affecting electrostatic assembly of biopolymer particles fabricated from gelatin and pectin

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ABSTRACT

Hydrogel microspheres may be used for various applications within foods, cosmetics, and pharmaceuticals, such as texture modification, encapsulation, or controlled release. The aim of this research was to examine the key parameters affecting the formation and properties of hydrogel microspheres fabricated by electrostatic complexation of gelatin and pectin. Hydrogel microspheres were formed by mixing 0.5 wt% gelatin and 0.01 wt% pectin at pH 10.0 and 30 °C, and then acidifying to pH 5.0 with continuous stirring. The effects of salt content (0–100 mM NaCl), shear rate (150–600 rpm), and acidification rate (fast, medium, and slow) on the formation and properties of the hydrogel microspheres were investigated. Increased salt content perturbed the complexation process due to electrostatic screening and ion-binding effects, which meant that lower pH values were needed to induce complexation. Optical microscopy and static light scattering showed that salt content also altered hydrogel particle microstructure. The largest particles were formed at an intermediate shear rate (300 rpm), which was attributed to the influence of shearing on mixing, particle disruption, and particle coalescence. Hydrogel microsphere size decreased as the acidification rate increased, which was attributed to an alteration in the balance of particle formation and particle growth. The parameters identified in this study facilitate the design of hydrogel microspheres with specific sizes and morphologies, which might be useful for tailoring their functional properties for different commercial applications.

1. Introduction

In general, hydrogel microspheres may be useful for a variety of applications within the food, personal care, and pharmaceutical industries (Kashyap, Kumar, & Kumar, 2005; Matalanis & McClements, 2013; Shewan & Stokes, 2013; Vashist, Vashist, Gupta, & Ahmad, 2014). They can be used to encapsulate, protect, and release bioactive agents, such as nutraceuticals, cosmetics, or pharmaceuticals. They may also be used to modulate the appearance, rheology, and stability of aqueous solutions due to their ability to scatter light, alter fluid flow, and increase viscosity. In this study, we focused on the potential application of hydrogel microspheres to replace fat droplets and starch granules in foods.

Overweight and obesity have become major contributors to the global increase in certain chronic diseases in both developed and developing nations, e.g., heart disease, hypertension, and diabetes (Malik, Willett, & Hu, 2013). The ultimate causes of obesity and overweight are a lack of physical activity and a high calorie intake from the diet (Malik et al., 2013; Wu, Degner, & McClements, 2013). The negative impact on the quality of human life, as well as the reduction in economic productivity and increase in health care costs, associated with overweight and obesity have led to increased demands from consumers and governments for reduced-calorie foods (Buttriss, 2013; Transparency Market Research, 2014). The relatively high caloric density of fat has made it a major target for the development of low-calorie foods (Wu, Degner, & McClements, 2014). However, the potential link between the intake of refined carbohydrates (such as starch and sugar) and the risk of obesity and diabetes has also made refined carbohydrates a target for low-calorie products (Lustig, Schmidt, & Brindis, 2012; Malik et al., 2013). However, the removal of fat or starch from many food products (such as dressings, desserts, and sauces) compromises their physicochemical properties and sensory attributes, e.g., appearance, texture, stability, and mouthfeel (Nehir El & Simsek, 2012; van Aken, Vingerhoeds, & de Wijk, 2011). Therefore, it is necessary to develop effective approaches to remove fat droplets and starch granules from foods without adversely affecting their desirable properties or introducing potential new health problems (such as hypertension due to increased salt intake).

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Our previous work demonstrated the potential of using hydrogel microspheres formed from gelatin and pectin to replace fat and starch granules (Wu et al., 2014). These hydrogel particles can be formed *via* electrostatic complexation (Fig. 1). Solution conditions are manipulated so that the gelatin and pectin molecules associate with each other through electrostatic attraction, which leads to phase separation into a polymer-rich phase and a polymer-depleted phase. When this system is stirred it separates into a water-in-water emulsion with the polymer-rich phase forming the disperse phase (hydrogel particles) and the polymer-depleted phase forming the continuous phase (Turgeon & Laneuville, 2009; Turgeon, Schmitt, & Sanchez, 2007; Wu et al., 2014). These hydrogel particles may be promising candidates for the development of healthy reduced-calorie foods because they are assembled from proteins and dietary fibers. Proteins (4 kcal/g) and dietary fibers (~0 kcal/g) have a much lower caloric density than fats (9 kcal/g), and may be more effective at inducing satiety than starch and fats, which may help reduce overall food consumption (Halford & Harrold, 2012). In addition, we have previously demonstrated that the hydrogel particles formed had similar rheological properties as starch granules, which may be important for delivering similar textural properties (Wu et al., 2014).

Previous studies have utilized similar biopolymers to improve the textural properties of reduced-fat products; however, most of these have used either gelatin or pectin alone as a thickener or they have formed macroscopic gels using gelatin and pectin (Cheng, Lim, Chow, Chong, & Chang, 2008; Knarreborg & Nielsen, 2012; Liu, Zhu, Xu, Guo, & Jin, 2007; Park, Hong, Kim, Choi, & Min, 2006; Wendin, Solheim, Allmere, & Johansson, 1997). To the best of our knowledge, the use of gelatin–pectin hydrogel beads as starch or fat mimetics has not been reported before. The spherical shape of these micron-sized hydrogel beads is of particular interest because it may impart unique rheological properties that cannot be achieved by a single biopolymer or a bulk gel (Wolf, Frith, Singleton, Tassieri, & Norton, 2001). At low concentrations, hydrogel particle suspensions possess similar rheological properties as biopolymer solutions with the viscosity increasing with increasing biopolymer concentration (Shewan & Stokes, 2013). At high concentrations, the hydrogel particles become closely packed so that the suspension resembles a macroscopic polymer gel exhibiting viscoelastic properties (Dennin, 2008; Shewan & Stokes, 2013; van Hecke, 2010). However, unlike macroscopic polymer gels, the particle nature of these hydrogel microspheres allows them to slip against each other when the shear stress exceeds the yield stress (Dennin, 2008; Menut, Seiffert, Sprakel, & Weitz, 2012; van Hecke, 2010). This jamming transition resembles that of highly concentrated food emulsions in full fat products or highly concentrated starch suspensions containing swollen granules (Fernández Farrés, Moakes, & Norton, 2014; Menut et al., 2012; Wu et al., 2014). Consequently, the hydrogel microspheres developed in this study may have applications as fat or starch mimetics. The rheological properties of suspensions of hydrogel particles are largely affected by the microstructures of the hydrogel particles in the system, including the particle shape, size and size distribution (Fernández Farrés et al., 2014; Menut et al., 2012; Shewan & Stokes, 2013; Wolf et al., 2001). This in turn has important consequences on the mouthfeel attributes of the products, e.g., roughness, slipperiness, creaminess, etc. (Prinz, Wijk, & Weenen, 2005; Weenen,

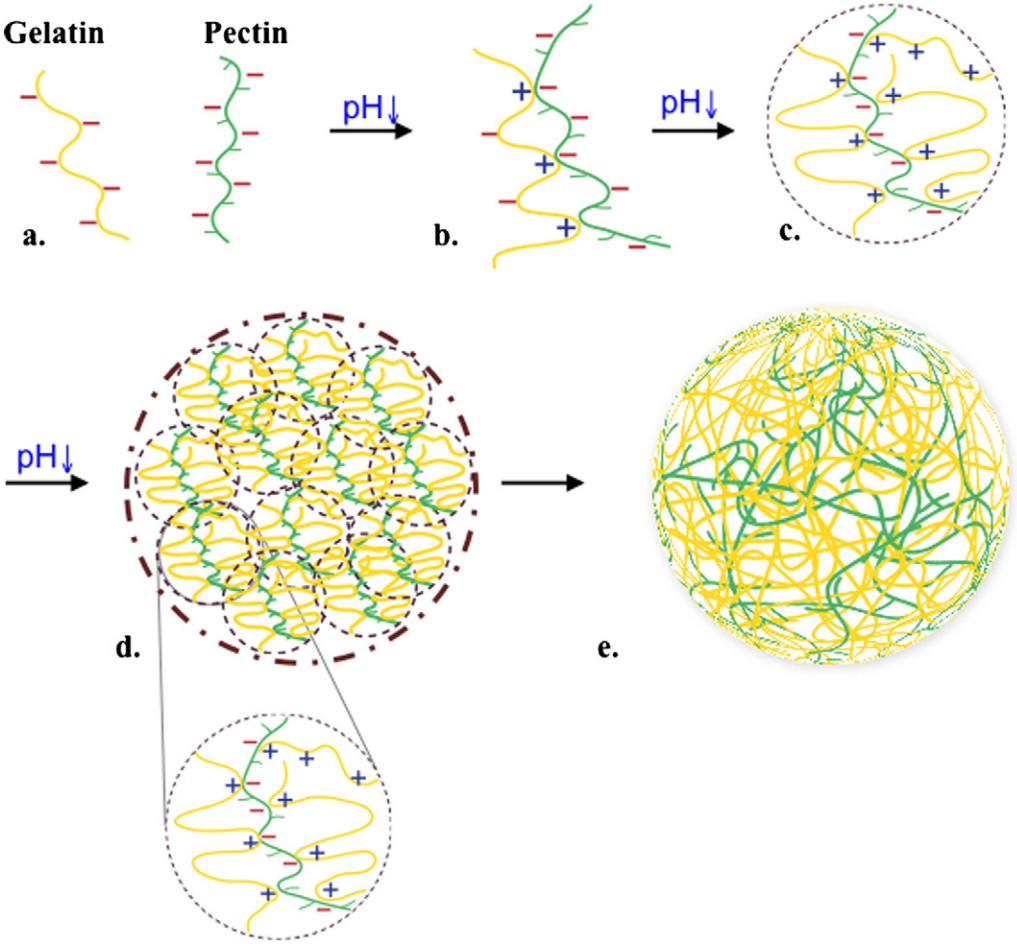

Fig. 1. Schematic illustration of the electrostatic complexation that occurs during acidification of gelatin and pectin mixtures (a) gelatin and pectin molecules exist as individual molecules in solution due to electrostatic repulsion; (b) gelatin–pectin soluble complexes are formed due to electrostatic attraction between positive patches on gelatin and negative patches on pectin; (c) soluble complexes merge and form gelatin–pectin sub-units; (d) hydrogel particles form due to coalescence of sub-units; and (e) setting of internal structure as temperature cools down.