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Development of hydrocolloid microgels as starch granule mimetics: Hydrogel particles fabricated from gelatin and pectin

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ABSTRACT

In this study, hydrocolloid microgels fabricated by electrostatic complexation of gelatin and pectin were developed as possible starch mimetics. The impact of covalent cross-linking on the physicochemical and structural properties of the microgels was investigated. Microgels were formed by acidifying a mixture of gelatin (0.5 wt.%) and pectin (0.01 wt.%) from pH 10 to 5 at 40 °C, followed by cross-linking with glutaraldehyde (0 to 2 mM). At low glutaraldehyde levels (<0.5 mM), cross-linking occurred primarily within the microgels and did not affect particle dimensions, whereas at high levels (2 mM), cross-linking connected adjacent microgels leading to the formation of large flocs. Rheological and microscopic analysis showed that the degree of cross-linking impacted the thermal transitions of the microgels. A simulated oral processing study indicated that the melt-in-the-mouth behavior of the hydrocolloid microgels could be made to be similar to that of starch granules by controlling the degree of cross-linking. This study may be useful for designing starch mimetics with improved texture-modifying properties and reduced-calories.

1. Introduction

The food industry is interested in developing high-quality food and beverage products with reduced-calorie contents to combat health problems associated with overweight, obesity, and diabetes. Fat has the highest calorie density of the major macronutrients (fat, carbohydrates, and proteins) and therefore has been a primary target for calorie reduction in the food industry (McClements, 2015). Nevertheless, the removal of fat from many foods is challenging because it makes a major contribution to their desirable appearances, textures, mouthfeel, and flavor profiles. For this reason, there has been considerable interest in the development of fat mimetics that can replace some of the desirable attributes that are lost when the fat is removed. Starch granules have been widely used as fat mimetics in many emulsion-based products, such as dressings, sauces, yogurt, dips, and desserts (Beggs, Bowers, & Brown, 1997; Mounsey & O'Riordan, 2008; Sandoval-Castilla, Lobato-Calleros, Aguirre-Mandujano, & Vernon-Carter, 2004; Sikora, Badrie, Deisingh, & Kowalski, 2008). However, ingestion of high levels of digestible carbohydrates has recently been linked to the prevalence of diabetes, overweight, and obesity in many developed countries (Lustig, Schmidt, & Brindis, 2012; Walker & Parker, 2014). For this reason, there is now interest in also replacing digestible starches with low-calorie starch mimetics. These starch mimetics should be capable of providing similar physicochemical and sensory attributes to foods as conventional starch ingredients normally would (such as appearance, texture, and mouthfeel), but they should contribute fewer calories.

There are two important attributes of modified starch granules that have made them a popular fat mimetic. First, swollen starch granules are highly effective at increasing the viscosity of food systems (Rao, 2014). Second, starch granules are hydrolyzed by α-amylase in the saliva, which contributes to the desirable textural perception of foods (Butterworth, Warren, & Ellis, 2011). In particular, the disintegration of starch granules within the mouth leads to a melting sensation that contributes to creaminess perception (Sarkar & Singh, 2012; Weenen, 2005). As mentioned earlier, overconsumption of starch has raised some health concerns. First, starch may not be as satiating as fat and therefore leads to overeating, which may actually contribute to an increase in obesity (Stubbs, Mazlan, & Whybrow, 2001; Walker & Parker, 2014). Second, the rapid digestion of starch causes a sudden rise in blood glucose levels which may pose a risk for diabetes (Van Kleef, Van Trijp, Van den Borne, & Zondervan, 2012). Consequently, it would be useful to develop a starch mimetic that could provide similar functionalities as starch granules (such as thickness and "melt in the mouth" behavior), but with more desirable nutritional attributes

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(such as lower calories and glycemic index) (Wu, Degner, & McClements, 2014).

Our previous studies (Wu et al., 2014; Wu & McClements, 2015a) have demonstrated the potential of using gelatin-based hydrogel particles to replace swollen starch granules. These hydrogel particles were assembled from positively charged proteins and negatively charged polysaccharides using electrostatic complexation. Under optimized solution conditions (*e.g.*, pH, ionic strength, temperature, and shearing), the two biopolymers associate with each other and form a water-in-water emulsion with a polymer-rich dispersed phase and a solvent-rich continuous phase (Turgeon & Laneuville, 2009; Turgeon, Schmitt, & Sanchez, 2007; Wu et al., 2014). Gelation of the polymer-rich dispersed phase leads to the formation of hydrogel particles or microgels that have similar dimension as starch granules, and therefore provide a similar thickening effect (Wu et al., 2014). In addition, the ingredients used for the fabrication of these microgels have relatively low caloric density (protein = ~4 kcal/g and dietary fiber = ~0 kcal/g), and should therefore be suitable for creating reduced-calorie starch mimetics. Finally, microgels fabricated from gelatin and pectin have a melting temperature below body temperature (Wu & McClements, 2015b), which may be useful for mimicking the "melt-away" mouth-feel of starch granules.

Nevertheless, there are still some technical challenges that need to be addressed when developing this type of starch mimetic. In particular, the relatively low melting temperature of pectin–gelatin microgels make them sensitive to thermal fluctuations that they might experience during food manufacturing, storage, and utilization. A major objective of the current study was therefore to examine the impact of covalent cross-linking of microgels on their thermal melting behavior. As a proof of principle, the hydrocolloid molecules within the microgels were cross-linked using a chemical agent: glutaraldehyde (Migneault, Dartiguenave, Bertrand, & Waldron, 2004). Glutaraldehyde can be used in certain food applications, provided that there is no residue remaining in the final product, which would have to be established. In commercial practice, other types of cross-linking agents could be used, such as the food-grade enzymes transglutaminase and laccase (Zeeb, Fischer, & Weiss, 2014). The effect of cross-linking on the microstructure and rheology of the microgels was investigated using simulated oral processing conditions, and their performance was compared to that of starch granules under similar conditions to establish their potential as starch mimetics.

2. Experimental methods

2.1. Materials

Acid-processed gelatin derived from porcine skin (Type A, 30 mesh granule size, and 100 Bloom strength) was provided by Gelita USA (Sergeant Bluff, IA). Citrus pectin (Pectin LM35, degree of esterification: 29%) was donated by TIC gum (White Marsh, MD). Modified starch derived from waxy corn starch (hydroxypropyl distarch phosphate) was a gift from Tate & Lyle (Hoffman Estates, IL). Porcine pancreas α-amylase (Type I-A, in PMSF treated saline suspension, Lot# SLBD9572V), mucin from porcine stomach (type II), ammonium nitrate, potassium phosphate, potassium chloride, potassium citrate, uric acid sodium salt, urea, lactic acid sodium salt, hydrochloric acid, sodium hydroxide, and sodium azide were purchased from Sigma-Aldrich (St. Louis, MO). Glutaraldehyde solution (25%) was purchased from Thermo Fisher Scientific (Waltham, MA).

2.2. Preparation of starch paste

A weighed amount of modified starch (7 g) was dispersed into double distilled water (93 g) and stirred for 30 min to allow hydration. Subsequently, the suspension (100 g) was placed in a 150 g beaker and heated to 90 °C in a water bath (MGW Lauda KS6, LAUDA, Lauda-Königshofen, Germany) and held for 5 min. The sample was stirred manually to allow even distribution of heat during the thermal treatment. After heating, the starch paste was immediately cooled to room temperature (25 °C) using an ice-water bath. The moisture loss during the heat process was compensated for by adding back double distilled water.

2.3. Preparation of gelatin–pectin electrostatic complexes

2.3.1. Stock solutions preparation

Gelatin stock solution (2 wt.%) was prepared by dispersing gelatin powder in double distilled water at 35 °C with continuous stirring for 1 h. Pectin stock solution (1 wt.%) was prepared by dispersing pectin powder in double distilled water and stirring overnight at room temperature for complete hydration. The stock solutions were mixed with sodium azide (0.02 wt.%) and stored at 4 °C to prevent microbial growth.

2.3.2. Gelatin–pectin complex formation

Aqueous solutions containing gelatin–pectin electrostatic complexes were prepared following similar procedures as those described previously (Wu & McClements, 2015a), but in this case different levels of cross-linking agent were included (0–2 mM glutaraldehyde). Gelatin stock solution was heated at 40 °C for 30 min to ensure it was in the random coil (liquid) state. The pH value of the stock solutions containing gelatin, pectin, and double distilled water were first adjusted to pH 10.0 using NaOH solutions (2 and 1 M). Subsequently, a gelatin–pectin mixture (pH 10, 1600 g) was prepared by mixing weighed amounts of the stock solutions and pH-adjusted double distilled water to obtain a final concentration of 0.5 wt.% gelatin and 0.01 wt.% pectin. The mixtures were then heated to 40 °C with continuous stirring at a shear rate of 300 rpm (Fisher Scientific Isotemp Basic Stirring Hotplates, Fisher Scientific, Pittsburgh, PA). When the temperature was stabilized, a total of 3100 μL of 1 M HCl solution was titrated into the mixture at a rate of 50 μL per 30 s using an automated electronic pipette (Rainin SE4, Mettler Toledo, Oakland, CA). As a result the biopolymer mixture reached a final pH of 5. The required amount of 0.1 M HCl was determined in a preliminary experiment. Once the pH value was adjusted, a fixed volume of 2.5 M glutaraldehyde was titrated into the mixture to reach final cross-linking agent concentrations ranging from 0.1 to 2 mM. A mixture without glutaraldehyde was prepared as a control. The total heating time after pH adjustment was 20 min for all the samples. The mixtures were then cooled in an ice-water bath to 25 °C and were kept stirring at 300 rpm at room temperature prior to further analysis. The pH and temperature of the samples were monitored using a pH meter (Metrohm® 827 pH Lab Meter, Metrohm, Riverview, FL). All the mixtures were prepared in a 2000 mL beaker and were stirred using magnetic stir bars (Octagonal, 0.5 in. diameter; 3 in. length, Thermo Fisher Scientific, Waltham, MA). After formation the hydrogel beads were stored for 24 h at ambient temperature prior to analysis. Previous studies have reported that the majority of cross-linking in polysaccharide-gelatin hydrogels occurs within the first 2 h, and therefore we assumed that the microgels were full hardened prior to further analysis (Buhus, Popa, & Desbrieres, 2009).

2.3.3. Collection of hydrogel particles

The hydrogel particle dispersions were centrifuged at 6000 rpm at 25 °C for 40 min using a centrifuge (Sorvall RC6 Plus, Thermo Scientific, Agawam, MA) with a fixed-angle rotor (Fiberlite, PIT F10S-6 × 500Y, Santa Clara, CA). After centrifugation, the supernatant was discarded and the centrifuge bottles were inverted for 3 min to remove excess supernatant from the sediment. Subsequently, the sediment which consisted of the gelatin–pectin complex, was collected for rheological and microscope analysis.