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Beverage emulsions: Comparison among nanoparticle stabilized emulsion with starch and surfactant stabilized emulsions

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ABSTRACT

Emulsions are widely used in beverages to impart desired appearance and flavor to the products. Ring formation in beverages with emulsions during thermal processing and storage is one of the key challenges. This study was aimed at comparing the relative effectiveness of silica nanoparticle based emulsifiers with surfactant and biopolymer based emulsifier (modified starch) in influencing physical stability of emulsions in a model juice. The stability of emulsions was measured by characterizing changes in emulsion droplet size, zeta potential, UV–vis absorbance and visual evaluation of phase separation or ring formation in both primary emulsions and beverage emulsions as a function of storage time. The influence of thermal processing on stability of emulsions both immediately after processing and upon storage was evaluated. The thermal processing conditions simulated both high temperature short time and low temperature long time pasteurization conditions. The results demonstrate that the mean droplet diameter of primary emulsions stabilized by selected emulsifiers was stable during storage for 21 days with and without pasteurization. Based on measurements of mean droplet diameter and visible ring formation, polyoxyethylene sorbitan monolaurate (tween-20) stabilized emulsion was not stable in a model juice and the stability of this emulsion was further reduced with thermal processing. In contrast, starch and silica stabilized emulsions in a model juice did not show significant changes in particle diameter or visible ring formation during storage with and without prior thermal processing, although starch stabilized emulsion did show a decrease in absorbance during storage. Zeta potential measurements in a model juice indicate that the surface properties of emulsions were significantly distinct from those of primary emulsion, indicating interaction of juice components with the emulsion interface influencing the surface charge at the interface. These changes in zeta potential of emulsion droplets did not correlate with reduced stability of the emulsions. Overall, the results demonstrate that nanoparticle stabilized emulsions can improve stability of emulsion in beverages as compared to surfactant and biopolymer stabilized emulsions and provides a comprehensive matrix to evaluate stability of emulsions in beverages.

1. Introduction

Emulsions are commonly used in beverage products including juice and soft drinks to influence flavor, appearance and color of the product (Buffo, Reineccius, & Oehlert, 2001; Given, 2009). Instability such as phase separation of the emulsion in beverage products can influence flavor and color profile and limit the shelf life of the product. Significant research efforts are being made to select optimal formulations of biopolymer emulsifiers to improve stability of emulsions in beverage products (Piorkowski & McClements, 2013). This research has been motivated by the understanding that selection of optimal emulsifier influences both the diameter of emulsion droplets and stability of emulsion. Currently, polysaccharides such as gum Arabic and modified starch are commonly used as emulsifiers for beverage emulsions. These polysaccharide based emulsifiers are preferred compared to globular proteins and other small molecule emulsifiers because the latter are more sensitive to environmental conditions (pH, ionic strength, temperature) (Chanamai & McClements, 2002) and may also influence the flavor profile of the product (McClements, 1998). Gum Arabic is derived from *Acacia senegal* and consists of various polymer fractions (Anderson, Howlett, & Mcnab, 1985; Goodrum, Patel, Leykam, & Kieliszewski, 2000). The hydrophobic fractions of gum Arabic molecules stabilize an oil droplet in water by anchoring to the oil surface while the hydrophilic fraction of the biopolymer extends into water and stabilize the oil droplet by steric hindrance and electrostatic repulsion (Chanamai & McClements, 2000). Modified starch has also been used for stabilization of beverage emulsions. Since the natural starch backbone is hydrophilic, chemical modification such as octenylsuccinic acid modification of natural starch is carried out to introduce

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hydrophobic groups for stabilization of the beverage emulsions (Trubiano, 1995). This modification has been FDA approved for use in food. OSA starches have also been approved as food additive in the EU (E1450). The hydrophobic sections, as a result of modification, anchor the starch molecule to the oil droplet surface, while the hydrophilic starch chains stick out into the aqueous phase and protect droplets against aggregation through steric repulsion (Tesch, Gerhards, & Schubert, 2002).

Despite significant application of polysaccharides in beverage emulsions, there are some limitations of the polysaccharide based emulsifiers used for stabilizing beverage emulsions. For stable emulsion formation, gum Arabic has to be used at relatively high concentrations. For example, 20% gum Arabic is required to stabilize 12.5% oil-in-water (O/W) emulsion (Chanamai & McClements, 2002). Similar to gum Arabic, modified starch also have low interfacial activity (Piorkowski & McClements, 2013). Therefore, relatively higher concentration of starch as compared to conventional surfactants such as polyoxyethylene sorbitan monolaurate (tween-20) is required to form stable emulsions. As a result, a significant fraction of gum Arabic or starch remains dispersed in the aqueous phase and is not absorbed at the oil–water interface in an emulsion. These non-absorbed molecules can influence stability of emulsions as studies have shown that non-adsorbed molecules can increase the attractive forces between oil droplets due to an osmotic effect (Chanamai & McClements, 2001). These interactions between the emulsion droplets and the unabsorbed biopolymer can result in flocculation of the oil droplets. Another potential issue with the use of gum Arabic is the reliability of the supply chain and natural variance in the composition of gum Arabic (Garti, 1999).

In contrast to biopolymer based stabilizers, nanoparticles can also stabilize oil droplets in water and form emulsions that are known as the Pickering emulsions (Chevalier & Bolzinger, 2013; Pickering, 1907). The unique advantage of the Pickering emulsion is the near irreversible adsorption of nanoparticles at the oil–water interface in contrast to highly dynamic interfacial properties of the biopolymer emulsifiers (Tcholakova, Denkov, & Lips, 2008). The restricted movement of the nanoparticles compared to the biopolymer emulsifiers is expected to improve stability of the emulsions. Particle stabilized emulsions are commonly used in manufacturing of food products such as mayonnaise, salad dressing, yogurt, whipped products, etc. (Leal-Calderon, Thivilliers, & Schmitt, 2007) and are known to be efficient stabilizers for these applications (Leal-Calderon & Schmitt, 2008). Synthetic (organic and inorganic) as well as biological particles can be used for stabilizing emulsions (Boker, He, Emrick, & Russell, 2007). In this study, we chose silica particles for stabilization of the beverage emulsion as silica nanoparticles can stabilize emulsion droplets over a large range of pH conditions (Midmore, 1998) which is a prerequisite for beverage applications. Therefore, emulsions stabilized by silica particles are suitable for beverage applications. Furthermore, significant research has been done to form silica nanoparticles with precise control on size, surface chemistry that can be used in many food and cosmetic formulations (Gibbs, Kermasha, Alli, & Mulligan, 1999; Schutt, Klein, Mattrey, & Riess, 2003; Tikekar, Pan, & Nitin, 2013; Zhao, Dan, Pan, Nitin, & Tikekar, 2013).

The overall goal of this study was to compare the stability of a silica stabilized Pickering emulsion as compared to the emulsions stabilized using a non-ionic emulsifier such as tween-20 and a polysaccharide emulsifier such as octenyl succinic anhydride modified starch in a model pear juice. Tween-20 is a non-ionic surfactant while modified starch is a relatively large MW (avg. Mw ~ 10^6–10^7 Da) biopolymer. Many juice products including the model pear juice as used in this study are acidic in nature. It was hypothesized that the beverage emulsion stabilized by inorganic silica particles provides better stability to the emulsion in the acidic environment of the juice. In this study, stability of the emulsion in a model beverage product was determined by in-situ monitoring of emulsion mean droplet diameter and zeta potential of the droplets. Since pasteurization of beverage products may be desirable for extended shelf life and for elimination of pathogens, stability of the primary emulsion and the beverage formulation with emulsion was also evaluated after pasteurization. The results of this study will highlight the potential of nanoparticle based emulsifier for stabilization of oil droplets in beverage products.

2. Materials and methods

2.1. Materials

Tween-20, silica (LUDOX® CL colloidal silica) and citric acid (anhydrous) was purchased from Sigma-Aldrich (St. Louis, MO, USA). The colloidal silica was supplied as 30 wt.% suspension in water. The silica particle size in the given suspension is 20 nm and zeta potential is +40 mV. Starch (CAPSUL® TA) and sodium benzoate were obtained from the National Starch Food Innovation (Bridgewater, NJ, USA) and Fisher Scientific (Hampton, NH, USA) respectively. CAPSUL® TA is an octenyl-succinate anhydride starch, which is made by esterification of starch and anhydrous octenylsuccinic acid under alkaline conditions. The degree of modification is less than 3%. High fructose corn syrup 55 (HFCS) with 77% solids, pear juice concentrate and medium chain triglyceride (oil) was gifted by Dr. Pepper Snapple Group (Plano, TX). Ultrapure water (16 MΩ cm) was obtained from an in-house water filtration system and used as is for all the experiments. All the materials were used as is until and unless mentioned otherwise.

2.2. Beverage emulsion preparation

The concentrations mentioned are w/w until and unless mentioned otherwise. Tween-20 (2%), starch (5%) and silica (5%) solutions were prepared in ultrapure water with 0.2% citric acid and 0.3% sodium benzoate. Sodium benzoate was included in the formulation in order to avoid microbial growth in the emulsion during storage. Coarse emulsions were prepared by dispersing 5% oil (medium chain triglyceride) in tween-20, starch or silica solutions using a hand-held disperser (Ultra-Turrax, model T25, IKA Works, Wilmington, NC) set at 24,000 rpm for 2 min. These coarse emulsions were subsequently homogenized by a probe sonicator (Q55, QSonica, Newtown, CT) for 30 s at amplitude of 50% to achieve uniform droplet diameter distribution. The pH of all the emulsions was measured and found out to be 4.

2.3. Model juice preparation

Model pear juice was prepared by mixing the following components in the mentioned concentrations: ultrapure water (84%), HFCS (14%), citric acid (0.25%), sodium benzoate (0.3%) and pear juice concentrate (1%). The mixture was stirred at 1000 rpm for 10 min. The emulsion (0.05%) was mixed with the model juice. The pH of the model pear juice with emulsion remained unchanged (pH = 4).

2.4. Pasteurization conditions

Pasteurization of primary emulsions and model juice was carried out at 2 different conditions: 70 °C for 30 min and 90 °C for 3 min. Pasteurization was performed in a water bath at atmospheric pressure without agitation of the samples.

2.5. Mean droplet diameter and zeta potential measurement

Hydrodynamic diameter and zeta potentials of oil droplets in primary emulsions as well as in model juice were measured using a particle size analyzer (Model: Malvern Nano Series; Malvern Instruments, Inc., Westborough, MA). Primary emulsions were diluted 100× in water prior to mean droplet diameter measurement. Emulsion mean droplet diameter in model juice was measured without further dilution. For diameter measurements, the analyzer was set to following specifications: