Effectiveness of encapsulating biopolymers to produce sub-micron emulsions by high energy emulsification techniques

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Abstract

In this study, different emulsifying ingredients were used to produce sub-micron emulsions for encapsulation purposes. Maltodextrin combined with a surface-active biopolymer (modified starch, or whey protein concentrate), or a small molecule surfactant (Tween 20) were used as the continuous phase, while d-limonene was the dispersed phase. Results showed that biopolymers are not efficient ingredients to produce very small emulsion droplets compared with small molecule surfactants because of their slow adsorption kinetics. The main problem with surfactants also is instability of the resulted emulsions due to "depletion and bridging flocculation" caused by free biopolymers and competition between surfactant and surface-active biopolymers. In general, it was not possible to produce a fairly stable microfluidized emulsion with surfactants for encapsulation purposes.
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1. Introduction

Emulsification is one of the important and critical steps in microencapsulation of food oils and flavours through spray drying and emulsion properties such as stability and droplet size[1] play a key role in optimizing the encapsulation efficiency during the process (Barbosa, Borsarelli, & Mercadante, 2005; Danviriyakul, McClements, Decker, Nawar, & Chinachoti, 2002; Liu, Furuta, Yoshii, & Linko, 2000, 2001; Risch & Reineccius, 1988). A stable emulsion with minimum droplet size can increase the retention of volatiles and shelf-life of encapsulated oil products through reduction of unencapsulated oil at the surface of powder particles (Ishido, Hakamata, Minemoto, Adachi, & Mat-suno, 2002; Minemoto, Hakamata, Adachi, & Matsuno, 2002; Soottitantawat, Yoshii, Furuta, Ohkawara, & Linko, 2003, 2005). So, sub-micron emulsions can be of real benefit for encapsulation purposes.

The production and control of submicron emulsions with a narrow size distribution have been attracting considerable attention in recent years. Nano-(submicron) emulsions are kinetically stable systems that can be transparent (EDS <200 nm) or "milky" (EDS ≈ 500 nm) (Izquierdo et al., 2002; Tadros, Izquierdo, Esquena, & Solans, 2004), and because of their very small EDS and high kinetic stability, they have been applied in various industrial fields, for example, personal care and cosmetics, health care, pharmaceuticals, and agrochemicals (Forgiarini, Esquena, Gonzalez, & Solans, 2001; Schulz & Daniels, 2000; Solans, Izquierdo, Nolla, Azemar, & Garcia-Celma, 2005; Sole, Maestro, Gonzalez, Solans, & Gutierrez, 2006; Sonneville-Aubrun, Simonnet, & L'Alloret, 2004). Production of nano-emulsions by "High-energy emulsification" methods like Microfluidization involves an application of very high

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[1] In rest of the discussion, instead of using different terms such as droplet diameter, droplet size, emulsion size, etc. which may become confusing, emulsion droplet size or simply EDS will be used.

amounts of energy (e.g., high pressures) on a previously prepared coarse emulsion to produce very small emulsion droplets. Some workers believe Microfluidization is superior because, EDS distributions appeared to be narrower and smaller in Microfluidized emulsions than in the traditional emulsifying devices (Dalgleish, Tosh, & West, 1996; Pinnamaneni, Das, & Das, 2003; Robin, Blanchot, Vuillemard, & Paquin, 1992; Strawbridge, Ray, Hallett, Tosh, & Dalgleish, 1995). It is shown, however, that Microfluidization is unfavourable in specific circumstances such as higher pressures and longer emulsification times, as it leads to "over-processing", which is re-coalescence of emulsion droplets (Jafari, He, & Bhandari, 2006a, in press; Lobo & Svereika, 2003; Olson, White, & Richter, 2004).

Final EDS is the result of equilibrium between droplet break-up and re-coalescence. Between new droplet formation and its subsequent encounter with surrounding droplets, emulsifiers adsorb onto the created interface to prevent re-coalescence. If the timescale of emulsifier absorption is longer than the timescale of collision, the fresh interface will not be completely covered and will lead to re-coalescence, i.e., an EDS increase (Desrumaux & Marcand, 2002; Kolb, Viardot, Wagner, & Ulrich, 2001; Marie, Perrier-Cornet, & Gervais, 2002; Perrier-Cornet, Marie, & Gervais, 2005). Fast stabilization of new interfaces by sufficient emulsifier molecules is an efficient way to prevent re-coalescence (Brosel & Schubert, 1999; Floury, Desrumaux, Axelos, & Legrand, 2003; Karbstein & Schubert, 1995; Schulz & Daniels, 2000; Stang, Karbstein, & Schubert, 1994; Stang, Schuchmann, & Schubert, 2001). An effective emulsifier should adsorb rapidly at the fresh interface created during emulsification, reduce interfacial tension appreciably to facilitate droplet disruption, and prevent new droplets from flocculation by providing a protective layer around them.

There are many different emulsifiers available to incorporate into emulsions; some of them are solely emulsifier such as Spans and Tweens (Floury, Legrand, & Desrumaux, 2004; Marie et al., 2002) and some have both emulsifying and stabilising properties such as milk proteins and modified starches (Mohan & Narsimhan, 1997; Tesch, Gerhards, & Schubert, 2002). Slow emulsifiers, like biopolymers and high molecular weight surfactants can only be used effectively in emulsification systems with high residence times, such as colloid-mills, or multistage high pressure systems because, they get the chance to stabilize newly broken up droplets more than once. Small-molecule emulsifiers such as Tween 20 stabilize new interfaces in milliseconds, so that the droplets are unlikely to re-coalesce. When a mixture of emulsifiers is present, different molecules compete to adsorb at oil-water interface and lower the interfacial tension (Arboleya & Wilde, 2005; Dickinson, 2003; Klinkesorn, Sophanodora, Chinachoti, & McClements, 2004; McClements, 2004). Since low molecular weight surfactants are much smaller in size than biopolymers, and because they can reduce interfacial tension more efficiently and quickly by adsorbing a large number of molecules

within the same surface area, they are likely to dominate at the interface after equilibration, if both are present at high enough bulk concentrations (Kerstens, Murray, & Dickinson, 2006; Mackie, Gunning, Wilde, & Morris, 2000; Pugnaloni, Dickinson, Ettelaie, Mackie, & Wilde, 2004).

By the advent of modern emulsification systems and their potential application in encapsulation of food ingredients, understanding the mechanisms of emulsification and the behaviour of emulsion components along with the knowledge of factors affecting the emulsion properties during emulsification is essential. Also, there has been limited work to produce sub-micron emulsions with small molecule surfactants for encapsulation purposes. In fact, most of the published work in the emulsion territory is dealing with pure emulsions consisting water, oil and emulsifier. While in emulsification for subsequent encapsulation purposes, there is another constituent involved, so-called wall material or encapsulation matrix, which is mainly a biopolymer and has some direct and indirect influences on the emulsion properties. Therefore, the objectives of this work are to determine the optimum emulsification conditions and evaluate the influence of extreme emulsification conditions of Microfluidization on emulsion stability and droplet size by applying different surface-active biopolymers and surfactant.

2. Materials and methods

2.1. Materials

d-Limonene ($\rho = 840$ kg/m^3, $\eta = 8.8$ mPa s at 25 °C, RI = 1.487) was supplied by Quest International (NSW, Australia). Modified starch (Hi-Cap 100, waxy corn starch-modified, 5% moisture, solubility > 90%) and Maltodextrin (DE = 16–20, 5% moisture, bulk density = 600 kg/m^3) were purchased from National Starch and Chemical (Sydney, Australia), and Penford Limited (NSW, Australia), respectively. Whey protein concentrate (73% protein, 9% fat, 4% moisture, 5% lactose, 4% ash) was purchased from New Zealand Milk Products (ALACEN, Auckland, New Zealand). A non-ionic surfactant, i.e., Tween 20 (HLB = 16.7, $\eta = 350$ mPa s at 25 °C, RI = 1.468) was purchased from LabChem (NSW, Australia) and used as an added or a single emulsifying agent in some stages of this work. Analytical grade hydrochloric acid (HCL) and sodium azide (NaN$_3$) were purchased from Sigma Chemicals Company (Sydney, Australia). Distilled water was used for the preparation of all solutions. All general chemicals used in this study were of analytical grade.

2.2. Coarse emulsion preparation

All emulsions were produced in two stages, as described in our previous study (Jafari, He, & Bhandari, in press): (a) pre-emulsions were obtained with a rotor-stator system (L2R, Silverson Machines Ltd, UK). Silverson is a typical