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Stable water-in-oil emulsions formulated with polyglycerol polyricinoleate and glucono-δ-lactone-induced casein gels

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ABSTRACT

The destabilization of water-in-oil (W/O) emulsions greatly restricts their application. Converting the inner water droplets into soft solid-like gelled particles is an appealing strategy to improve the stability of W/O emulsions. In the present communication, we propose a novel method for preparing stable W/O emulsions containing gelled water droplets. In this method, the 3% (w/v) casein dispersions containing 0.9% (w/v) glucono-δ-lactone (GDL) and soybean oil with 2% or 6% lipophilic emulsifier polyglycerol polyricinoleate (PGPR) were homogenized to form W/O emulsions. Three hours later, the GDL-induced gelation of caseins in the inner aqueous phase occurred; thus, the W/O emulsions containing gelled water droplets were formed. The stability of the emulsions was characterized by Turbiscan analysis, particle size changes and visual inspection of phase separation. It was found that the W/O emulsions containing GDL-induced casein gels in the inner aqueous phase showed higher resistance to destabilization than the non-gelled W/O emulsions. In addition, the stability of the emulsions formulated by the gelled aqueous phase and 2% PGPR was even higher than emulsions with 6% PGPR in the absence of the gelled aqueous phase. These findings suggested that this method is an effective strategy for improving the long-term stability of W/O emulsions.

1. Introduction

Water-in-oil (W/O) emulsions can be employed as encapsulation and delivery matrices for water-soluble nutrients or drugs, such as peptides, proteins, vitamins and flavors (Nadin, Rousseau, & Ghosh, 2014). However, destabilization of W/O emulsions often occurs, which limits their application (Frasch-Melnik, Norton, & Spyropoulos, 2010; Márquez, Medrano, Panizzolo, & Wagner, 2010). Therefore, the development of relatively stable W/O emulsions to obtain W/O emulsions-based products of consistent quality during transport or storage is an important issue.

Due to the high mobility of water droplets, W/O emulsions are mainly destabilized by coalescence and sedimentation (Márquez et al., 2010). These destabilization processes can be partially inhibited by high concentrations of emulsifiers. W/O emulsions are often stabilized by synthetic low molecular weight or polymeric emulsifiers, such as polyglycerol polyricinoleate (PGPR) and sorbitan monostearate (Span 60). It is generally accepted that the use of synthetic emulsifiers in food or drug systems is strictly regulated (Dickinson, 2011). Moreover, the destabilization behavior (such as water transportation) of W/O emulsions-based products stabilized by high concentration of emulsifiers can not be efficiently avoided (Garti, 1997). Hence, many investigators continue to identify alternative methods to deal with the requirement for a high concentration of synthetic emulsifiers, while efficiently stabilizing the W/O emulsions (Andrés, Alejandra, Luis, & Jorge, 2010).

The incorporation of gelling biopolymers into the aqueous phase has been suggested as an effective way of improving the long-term stability of W/O emulsions, especially when the biopolymers added to the aqueous phase can form a network throughout the water droplet (Oppermann, Renssen, Schuch, Stieger, & Scholten, 2015). The mechanism(s) involved in this action has not been fully determined. It has been suggested the biopolymer gels in the inner aqueous phase show soft solid-like properties, making the inner water droplets more resistant to destabilization factors (Dickinson,

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2011; Massel, Alexander, & Corredig, 2015; Surh, Vladisavljević, Mun, & McClements, 2007; Weiss, Scherze, & Muschiolik, 2005).

However, the preparation of gelled biopolymer droplets in the oil phase is difficult due to rupture of the biopolymer gels into small droplets in the oil phase (Iancu, Chevalie, Popa, & Hamaide, 2009). Therefore, the preparation of these droplets is often carried out by inducing the gelation of biopolymers in the inner aqueous phase after the preparation of W/O emulsions. Some authors have proposed that gelation of the inner aqueous phase in W/O emulsions can be carried out by gelatin or heat denaturation of whey proteins (Oppermann et al., 2015; Surh et al., 2007).

Herein, we propose a new method of preparing W/O emulsions containing gelled water droplets without a high temperature process. The preparation of these emulsions is shown in the Graphical Abstract. Briefly, the oil (containing the lipophilic emulsifier PGPR) and casein dispersions (containing a certain amount of GDL) were homogenized to form W/O emulsions. Different to other acid reagents such as hydrochloric acid and sulfuric acid which totally dissociate the moment they are added to water, GDL is slowly hydrolyzed to gluconic acid and results in a gradual reduction in the pH of the inner aqueous phase within several hours. When the pH of the inner aqueous phase reaches the isoelectric point (pI = 4.6) of casein after ~3 h, gelation of the inner aqueous phase occurs (Supporting Materials SFig. 1). Thus, the W/O emulsions containing gelled water droplets are prepared. The objective of the present study was to examine this method, with special reference to the stability of W/O emulsions.

2. Materials and methods

2.1. Materials

The PGPR (Admul Wol 1403k) was purchased from Kerry Bio-Science (Norwich, New York, NY, USA). Caseinate sodium and GDL were purchased from Sigma Chemical Co. (St. Louis, MO, USA). Soybean oil (Fulinmen Co., Ltd., Tianjin, China) was purchased from a local supermarket and used without further purification. Deionized (18.2 MΩ) water was prepared using purification equipment (Sartorius Comfort I, Göttingen, Germany). All other chemical reagents used were of analytical purity.

2.2. Preparation of W/O emulsions

Caseinate sodium (3.0%, w/v) was fully hydrated in water using a magnetic stirrer for 12 h at 4 °C. Sodium azide (0.02%, w/v) was added to the casein dispersions to inhibit the microorganisms. Soybean oil and PGPR were mixed to obtain a content of 2.0 and 6.0 g PGPR in 100 g of the total oil phase, followed by heating at 45 °C for 2 min in a water bath to allow the PGPR to fully disperse in the oil phase. Then GDL (0.9%, w/v) was directly added into the casein dispersion (~25 °C). The dispersion was then magnetically stirred for 30 s to totally dissolve the GDL. The casein dispersion containing GDL should be used within 3 h of preparation.

To prepare the W/O emulsions, 90 ml casein dispersion (with 0.9% GDL or without GDL) or water (containing 0.9% GDL as the control) was slowly added to 270 ml oil over approximately 5 s, while mixing with an Ultra Turrax homogenization apparatus (IKA T 25, Staufen, Germany) with a dispersing head operating at 17,500 rpm for 1 min. The samples were then homogenized using a homogenizer at 60 MPa (NS1001 L-Panda 2K, Niro Soavi S.p.A., Parma, Italy). The prepared emulsions were stored at ambient temperature (~25 °C) for 24 h for further analysis.

2.3. Type and stability characterization of the W/O emulsions

The emulsions type was judged by observing the effects of several drops of the emulsions in both oil and water (Destribats et al., 2014). The W/O (O/W) emulsions can be fully dispersed in oil (water), but remains as drops in water (oil).

The stability of the emulsions was evaluated by three methods. The first was to monitor stability using the optical analyzer Turbiscan (Formulaction, L'Union, France). The Turbiscan is capable of detecting the destabilization behavior of a dispersed system much earlier and quicker than by the naked eye, especially for opaque systems (Araújo, Nikolic, Egea, Souto, & Garcia, 2011). A pulsed near-infrared light source and two synchronous detectors are positioned in the detection head, which moves up and down along a cylindrical cell to obtain data from transmission and backscattering. The measurements were performed every 30 min for 19 h at 25 °C. The curves delta backscattering was obtained by subtracting the backscattering profile at t = 0 from the profile at t. Global stability of the samples was evaluated by the Turbiscan stability index (TSI), which was calculated using the following formula:

$$TSI = \sqrt{\frac{\sum_{i=1}^{n} (x_i - x_{BS})^2}{n-1}} \quad (1)$$

where x_i is the backscattering for each measurement, x_{BS} is the mean of x_i, and n is the scan number.

The second method used to assess stability was size changes with time at ambient temperature. The first method in measuring the particle diameter was dynamic light scattering measurements (Horiba SZ-100, Kyoto, Japan). Highly concentrated samples were used to analyze the Z-average diameters with this device. All measurements were performed at 25 °C. The refractive index and viscosity introduced into the test condition were 1.473 and 52.4 mPa s, respectively. The refractive index and viscosity were measured by a refractometer (Anton Paar Abbemat 500, Ostfildern, Germany) and rheometer (TA Instruments Inc., New Castle, DE, USA), respectively. The second method used in measuring the droplet diameter was Turbiscan (Formulaction, L'Union, France), as used by some researchers (Abismaı, Canselier, Wilhelm, Delmas, & Gourdon, 2000). Three parameters were necessary when calculate the mean size of water droplets: dispersed phase refractive index, continuous phase refractive index and volume fraction. The refractive index of casein dispersions (without GDL) and pure water were 1.338 and 1.332, respectively. The refractive index of oil phase was 1.473. The volume fraction introduced to the calculating condition was 25%.

The third method was visual inspection of the appearance of phase separation following 90 days' storage after preparation of the emulsions. 10 ml emulsions was added to cylindrical bottles, sealed with rubber caps and stored at ambient temperature. The stability was evaluated by the sedimentation index (S), which was calculated using the following formula (Ushikubo & Cunha, 2014):

$$S(\%) = (H/H_0) * 100 \quad (2)$$

where H is the oil phase height at the top of the cylindrical bottles, H_0 is the initial height of the emulsions.

2.4. Statistical analysis

Experiments were independently performed three times. Statistical analyses of the data were carried out using IBM SPSS 21 for Windows 7.0. Duncan's multiple range tests for differences were applied.