Journal of Food Engineering 229 (2018) 12–20

Contents lists available at ScienceDirect

Journal of Food Engineering

journal homepage: www.elsevier.com/locate/jfoodeng

Investigation into the physicochemical stability and rheological properties of rutin emulsions stabilized by chitosan and lecithin

Ilyes Dammak*, Paulo José do Amaral Sobral

Department of Food Engineering, FZEA, University of São Paulo, Avenida Duque de Caxias Norte 225, 13635-900 Pirassununga, São Paulo, Brazil

ARTICLE INFO

Article history:
Received 17 April 2017
Received in revised form
18 September 2017
Accepted 23 September 2017
Available online 29 September 2017

Keywords:
Physicochemical stability
Lecithin
Chitosan
Degradation kinetic
Creaming

ABSTRACT

In this study, the possibility of producing stable O/W emulsions encapsulating rutin in oil droplets stabilized by soy lecithin and chitosan has been demonstrated. Emulsions were prepared using rotor-stator homogenization, which relied on the adsorption of cationic chitosan polymer to anionic oil droplet stabilized with lecithin. Results showed that emulsion stability index (*ESI*), mean droplet size ($d_{(3,2)}$), and rheological properties of emulsions were principally dependent on the chitosan concentrations. $d_{(3,2)}$ of emulsions was found increasing with the rise of chitosan concentration and reached a maximum value of 520 nm at 0.5% (w/w) chitosan. The emulsion destabilization over time was governed principally by coalescence and creaming instability mechanisms as demonstrated by Lumisizer' transmission profiles. All emulsions flow curves showed a near-Newtonian behavior as depicted by Power Law model results. Thermal degradation kinetics of rutin emulsions were studied at selected temperatures (4; 25; 40 °C). Chitosan concentration showed a good impact on the reduction of thermal degradation rate (k) of rutin emulsions during 30 days of storages, thus increasing rutin half-life ($t_{1/2}$). The lowest degradation rate occurred in the rutin emulsion stabilized with 2% (w/w) chitosan. Results indicated that the thermal degradation of rutin followed first-order reaction kinetics, and they could be expressed by Arrhenius equation. The activation energy value for rutin degradation was 27.8 kJ mol^{-1} with 2% (w/w) chitosan. These results implied that the physicochemical stability of rutin emulsions has been improved by addition of chitosan.

1. Introduction

Food emulsion stability is one of the most important factors governing the shelf life of emulsion products. The stability issues must be overcome before these products can be launched into market. Principally, emulsions are thermodynamically unstable systems and they tend to breakdown over time due to a number of different physicochemical mechanisms, which may occur concurrently such as creaming, flocculation, coalescence, phase inversion and/or Ostwald ripening (McClements, 2005; O'Dwyer et al., 2013). The kinetic stability of food emulsions is usually increased by using emulsifiers, which are surface-active ingredients that facilitate the generation of small droplets during homogenization by lowering the interfacial tension, and that improve emulsion stability by forming protective layer around droplets and/or by generating repulsive forces between droplets (Silva et al., 2015). Many commercially available food products are made up of emulsions, which are usually expected to remain stable for a reasonable period. However, interactions between these emulsions with other ingredients present within a food system may be very complex and will likely influence its stability (Dammak et al., 2017b). Therefore, it is the responsibility of the food manufacturers to develop products, which are kinetically stable at least within the period of its shelf life by preventing or retarding the breakdown mechanisms of the emulsions.

Small surfactants molecule (e.g. monoglycerides, polysorbates, sucrose esters, lecithin, etc.) are among the most commonly used emulsifiers for food processing (Tharwat, 2013). They facilitate the formation of emulsion and improve their stability by reducing the oil-water interfacial tensions and by forming a protective layer around the fat droplets to prevent them from aggregating. Nevertheless, some of these surfactants may not be able to provide sufficient long-term stability to the emulsions against flocculation and/or coalescence. In addition, some of these surfactants are incapable of withstanding hostile conditions such as elevated

* Corresponding author.
E-mail addresses: dammakilyes@usp.br, dammakilyes@hotmail.fr (I. Dammak).

https://doi.org/10.1016/j.jfoodeng.2017.09.022
0260-8774/

temperatures, freezing, chilling, dehydration, extreme pH and high mineral contents that may further aggravate the instability of the system (Guzey and McClements, 2006).

Hydrocolloids, for instance polysaccharides, are often incorporated into the oil-in-water (O/W) emulsions not only to create the desirable textural attributes, but also to stabilize the emulsion droplets against gravitational separation (Hanazawa and Murray, 2013). The ability of polysaccharides to enhance emulsion stability is attributed to different mechanisms, for example by lowering the interfacial tension, increasing the viscosity or forming a gel network in the continuous phase (Yu et al., 2013). In fact, when adsorbed at the oil-water interface, these hydrocolloids can be even more effective than surfactants and proteins in conferring long-term emulsion stability due to the formation of a thicker and stronger secondary layer favoring electrostatic and steric stabilization. Various studies have been reported on the use of polysaccharides to enhance the stability of O/W emulsions (Calero et al., 2013; Jia et al., 2015; Ye et al., 2017).

Chitosan is a natural cationic linear polymer, partially deacetylated derivative of chitin, that offers interesting properties to be used in foodstuffs due to its multifaceted properties such as biocompatibility, biodegradability, non-toxic nature, anti-hypercholesterolemic activity, antimicrobial activity, and film-forming properties (Luo and Wang, 2014; Nilsen-Nygaard et al., 2015). On the other hand, the ability of chitosan to trap dietary fat is widely reported in the literature, as a mean for controlling dietary fat absorption and controlling bodyweight (Rodriguez and Albertengo, 2005; Sugano et al., 1980). Using chitosan to stabilize or produce emulsions is attracting increasing attention (Alison et al., 2016; Dammak et al., 2017a; Wang et al., 2015). In most cases, chitosan acts as an emulsion stabilizer through the formation of an interfacial complex with absorbed surface-active agents (e.g. anionic surfactants or proteins) or through viscosity enhancement (Dickinson, 2010).

Rutin is a flavonoid belonging to the subclass of flavones and its antioxidant potential has been widely explored (Cushnie and Lamb, 2005; Vaquero et al., 2007). Rutin was found in many plants, such as buckwheat, rhubarb and asparagus (Yang et al., 2015). The high potential of the radical-scavenging activity of rutin makes it suitable as a good antioxidant, anti-inflammatory and anti-cancer agent (Perk et al., 2014). With these advantages, rutin could become a highlighted nutraceutical food product. However, rutin with a partition coefficient ($P_{octane/water}$) of 6.37 is highly hydrophobic with water solubility 0.0639 mg/mL (Das and Kalita, 2014). Encapsulation of rutin in O/W emulsions might overcame these limits, by improving the dispersibility of rutin and preventing its interaction with other compounds in food matrices.

Therefore, the purpose of this study was to study the effect of lecithin-chitosan addition on physicochemical stability of rutin oil-in-water (O/W) emulsions. Furthermore, we studied the rheological behaviors of rutin emulsions as function of chitosan concentration; and, we investigated the thermal degradation kinetics of rutin emulsions using First-order kinetic model and Arrhenius equation.

2. Materials and methods

2.1. Materials

Rutin hydrate (purity ≥ 94.0%) was purchased from Sigma-Aldrich (São Paulo, Brazil). Refined soybean oil was purchased from Cargill Agricola S.A. (São Paulo, Brazil). Soy lecithin (300 M, Caramuru) was bought from Prolabo (São Paulo, Brazil). Medium molecular weight chitosan (practical grade, batch STBF3507V, degree of deacetylation: 75–85%) was supplied by Sigma-Aldrich (São Paulo, Brazil). The water used was of Milli-Q quality with conductivity at 25 °C of 0.056 μS/cm.

2.2. Preparation of emulsions

The procedure of emulsion preparation is similar to our previous works (Dammak et al., 2017a). Briefly, the continuous phase was prepared by adding lecithin and chitosan to the water with different concentrations tested in this study. The dispersed phase was prepared by dissolving rutin in soybean oil at a concentration of 0.1% (w/w) with heating at 90 °C for 1 h. To study the effect of chitosan addition, different aqueous solutions of chitosan were prepared with final pH 3.0 (by adding acetic acid 1 M). Then, the chitosan solutions were added to the continuous phase. The weight ratio of dispersed phase to continuous phase of 1:9 was homogenized using a rotor-stator homogenizer (Ultra-Turrax® IKA T25, Labotechnik, Germany) at 10,000 rpm for 15 min. Prepared emulsions were cooled to room temperature before subsequent analysis.

2.3. Characterization of rutin emulsions

Mean droplet size ($d_{(3,2)}$) and emulsion stability index (*ESI*) of rutin emulsions were examined with the multi-sample analytical centrifuge (LUMiSizer, LUM GmbH, Berlin, Germany). LUMiSizer is based on the measurement of transmitted near infrared light (865 nm) as a function of time and position over the entire emulsion sample length simultaneously (Dammak and Sobral, 2017). The instrument simulates fast comprehensive emulsion destabilization due to the applied centrifugation force. The transmission profiles are displayed as a function of the radial position, as a distance from the center of rotation. The applied operating parameters were as follows: volume, 1.8 mL of emulsion sample; centrifugal force, 2325 × *g*; $time_{Exp}$, 6690 s; time interval, 30 s; temperature, 40 °C.

2.4. Droplets visualization

To visualize droplets shape, emulsions are sampled, diluted in the continuous phase, and tightly deposed on 76 × 26 × 1.2 mm rectangular concave glass slide and sealed with a coverslip. Samples were observed using a Carl Zeiss inverted microscope (Zeiss Axio Imager A2m, Germany) and visualized using an AxioCAM MRc digital camera. Images were processed using AxioVision Rel. 4.8 (Carl Zeiss, Jena, Germany) video acquisition/elaboration software.

2.5. Rheological properties of rutin emulsions

Rheological measurements were performed at 25 °C, with an AR2000 Advanced Rheometer (TA Instruments, West Sussex, UK), using cone and plate geometry (cone diameter = 16.0 mm, angle = 2°, gap = 2.0 mm). For each measurement, 2 mL of the emulsion was carefully deposited in the gap of the rheometer. All samples were allowed to rest for 5 min after loading to allow temperature equilibration and induced stress to relax. Steady-state flow measurements were carried out at 25 °C in the range of 1–100 s^{-1} during 5 min, and rheological parameters (shear stress, shear rate, viscosity) were obtained from the software Rheology Advantage Data Analysis V.5.3.1 (TA Instrument) (Dammak and Sobral, 2017). All characterizations were realized 3 times for each sample. Power Law model (Eq. (1)) was found suitable for fitting experimental data (Pevere et al., 2006):

$$\sigma = K\,\dot{\gamma}^{(n)} \tag{1}$$

where, σ is the shear stress (Pa), $\dot{\gamma}$ is the shear rate (s^{-1}), K is the