LWT - Food Science and Technology 76 (2017) 26–32

Contents lists available at ScienceDirect

LWT - Food Science and Technology

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

Emulsification process controlled by a mixer type rheometer in O/W protein-based emulsions

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ARTICLE INFO

Article history:
Received 27 July 2016
Received in revised form
15 October 2016
Accepted 18 October 2016
Available online 20 October 2016

Keywords:
Mixer type rheometer
Egg albumen
Emulsification
Viscosity
Droplet size distribution

ABSTRACT

In the present work, concentrated Oil-in-Water (O/W) emulsions were stabilized using egg albumen protein isolate as the only emulsifier. A helicoidal geometry was used and compared with a conventional one to assure an optimal emulsion preparation with that unusual geometry in order to come up with the utility of this rheometer as a valuable tool for understanding and controlling the emulsification process. The results put forward the importance of controlling the emulsification process to optimize the properties of the final emulsion and demonstrating a good agreement between in situ and off-line measurements obtained in mixer-type and conventional rheometers, respectively. Flow properties of the different emulsion prepared were measured, showing an increase in the viscosity with the agitation speed (from 10 to 16 to 114–117 Pa s), protein concentration (from 30 to 40 to 106–125 Pa s) and oil concentration (from 15 to 20 to 130–180 Pa s). Furthermore, the droplet size distribution (DSD) was also measured obtaining the influence of the different parameters with the Sauter diameter (a decrease from 20 to 30 to 7–8 μm, from 26 to 3 μm and from 17 to 24 to 8–14 μm was observed by increasing the agitation speed and the protein and oil concentration, respectively). The influence of the pH was also taken into account. Eventually, a relationship has been found that relates these properties to different composition (pH value, nature and concentration of proteins) or processing variables (agitation speed).

1. Introduction

An emulsifier is a surface-active specie, which are known to cover the interfaces lowering the interfacial tension favouring the formation of droplets (Hebishy, Buffa, Guamis, Blasco-Moreno, & Trujillo, 2015; Sánchez, Berjano, Guerrero, Brito, & Gallegos, 1998) and to delay the mechanisms of breaking down the emulsion (coalescence, flocculation, etc.) (Leal-Calderon, Schmitt, & Bibette, 2007; Walstra, 2003). Its presence is a key factor to require the long-term stability (Bengoechea, López, Cordobés, & Guerrero, 2009). Natural and commercial emulsifiers contribute surface activity that may alter the character of the emulsion (Hasenhuettl & Hartel, 2010). Proteins are widely used as emulsifier for oil-in-water (O/W) emulsions since they facilitate breakage of oil drops and prevent droplets coalescence over emulsification and storage (by increasing repulsion forces between droplets) (Dickinson, 2003; McClements, 2004; Ruttarattanamongkol, Nor Afizah, & Rizvi, 2015; Tcholakova, Denkov, Ivanov, & Campbell, 2006; Trentin, De Lamo, Güell, López, & Ferrando, 2011). Egg white albumen is selected as a model for studying the properties of protein-emulsions at the oil-water interface because it is frequently used as emulsion stabilizing agent (Kudryashova, Visser, van Hoek, & de Jongh, 2007; Niu et al., 2016). Some authors have used alternative proteins systems to stabilize O/W emulsions such as plant or fish proteins (Akintayo, Esuoso, & Oshodi, 1998; Cofrades, Carballo, Careche, & Colmenero, 1996; Dickinson & Lopez, 2001; Elizalde, Bartholomai, & Pilosof, 1996; Romero, Cordobés, Puppo, Guerrero, & Bengoechea, 2008).

The lifetime and stability of a final emulsion is strongly correlated to the droplet size distribution and the interactions between these particles in the dispersed phase (Melik & Fogler, 1988; Sánchez-González, Cháfer, Chiralt, & González-Martínez, 2010), the rheology of the continuous phase and the final pH of the emulsion because it alters the protein surface (which acts as the only emulsifier) and therefore, modifies the interfaces previously formed (Romero, Cordobés, & Guerrero, 2009). Those affect the flow of the emulsion, which is controlled by the flow index (n). Because n determines how the flow precisely develops, if $n < 1$ the fluid is called pseudoplastic, these fluids flow more easily by increasing shear rate (shear–thinning). The non-Newtonian fluids

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http://dx.doi.org/10.1016/j.lwt.2016.10.046
0023-6438/© 2016 Published by Elsevier Ltd.

are mostly pseudoplastic. On the other hand, when n > 1 the flow resistance increases with increased shear rate, and it is called a dilatant fluid (shear-thickenning) (Björn, Karlsson, Svensson, Ejlertsson, & de La Monja, 2012).

In addition, the emulsifying process plays an essential role in the final emulsion (McClements, 2005). Emulsification consists of dispersing one fluid into another, via creation of an interface. The emulsification process requires a considerable amount of energy to disperse one of the liquids in the form of small droplets in the continuous phase (Sánchez, Berjano, Guerrero, & Gallegos, 2001). Properties of an emulsion (stability, rheological properties, etc.) are governed not only by the presence of an emulsifier but also by the droplet size distribution (DSD) (Galus & Kadzinska, 2015; Leal-Calderon et al., 2007), so the process of emulsion formation is essential. Considering this formation process, mixer-type rheometers, which belong to the category of process rheometers, can be used because they allow the possibility to extract rheological information directly from a batch or semi-batch process during and after the preparation of complex products such as emulsions. The so-called Couette analogy may be used in order to transform the torque-rotor speed data into shear stress-shear rate curve (Ait-Kadi, Marchal, Chrissement, Choplin, & Bousmina, 2002).

The objective of this research was to characterize the protein-stabilized emulsions over and after processing by a mixer-type rheometer in order to put forward the utility of this rheometer as a valuable tool for understanding and controlling the emulsification process. In addition, a further objective of this work is to evaluate the influence of agitation speed, oil and protein concentrations and pH on the properties of egg albumen-based emulsions reached over and after emulsification and its stability. Therefore, characterization of the emulsions, particularly its viscosity and particle size distribution (Droplet Size Distribution, DSD), was carried out to accomplish this objective.

2. Materials and methods

2.1. Materials

Egg albumen powder containing ca. 850 g kg^{-1} protein was delivered by Proanda (Sevilla, Spain). Some physicochemical properties (protein solubility profile, free and total sulfhydryls, surface hydrophobicity and DSC) of this egg albumen concentrate have been reported in a previous paper (Félix, Martín-Alfonso, Romero, & Guerrero, 2014). Sunflower oil was purchased in a local market and used without further purification. Glycerol, used for calibration, was purchased from Sigma-Aldrich (France).

2.2. Emulsification process

The mixer-type rheometer consists of a cylindrical vessel equipped with a double helical ribbon impeller installed in a RS150 controlled stress rheometer (Nzihou, Bournonville, Marchal, & Choplin, 2004). Different O/W emulsions are prepared into the mixer-type rheometer (rotating at 5 rad/s) with an Ultra Turrax T-25 homogenizer from IKA. Emulsions were characterized in terms of three variables: the agitation speed during the emulsification process (5000, 10,000, 15,000 and 20,000 rpm), the emulsifier concentration (egg albumen protein in this case) (7.5, 15.0, 30.0 and 50.0 g kg^{-1}), the oil concentration (450, 550, 650 and 750 g kg^{-1}) and the final pH of the emulsion (3, 6 and 8). An emulsion prepared at 15,000 rpm and pH 3, 650 g kg^{-1} oil and 30 g kg^{-1} protein content was used as reference. The detailed emulsifying process consists of 30 s with only Ultra Turrax (UT) agitation, 420 s with UT homogenization and oil addition, followed by 60 s with UT agitation and 290 s without homogenization in order to stabilize the viscosity value.

2.3. Calibration of the mixer-type rheometer

The results were adjusted to the Ostwald de Waele or Power-law model, which is one of the methods known for explaining the behaviour of fluids. The model applies the following expression:

$$\eta = K\dot{\gamma}^{n-1} \tag{1}$$

where η is the apparent viscosity, $\dot{\gamma}$ is the shear rate and K and n are the consistency and flow index, respectively. Those parameters are included in an analytical method, based on the Couette analogy, to extract absolute viscosity-shear rate data in non-conventional geometries (Ait-Kadi et al., 2002; Nzihou et al., 2004), in particular that used in this study.

In the Couette analogy appears the constants K_τ (related to the torque) and Kγ (known as the Metzner-Otto constant, is related to the shear rate), which can be determined through a calibration procedure by using a Newtonian fluid (n = 1) of known viscosity (glycerol was used as Newtonian fluid). The expressions for these constants are the following:

$$\tau = K\tau \cdot T \tag{2}$$

$$\dot{\gamma} = K\gamma \cdot N \tag{3}$$

where τ and T are the shear stress and the torque (in N·m)

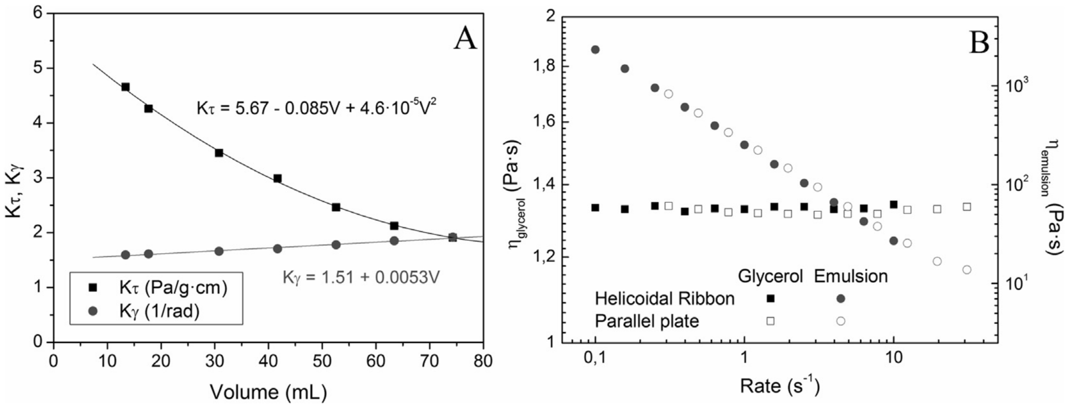

Fig. 1. (A) Evolution of constant values: related to the torque (K_τ) and shear rate (Kγ) in relation to the volume occupied by the sample and (B) viscosity values obtained with helicoidal ribbon (mixer-type rheometer) of glycerol (Newtonian fluid) and a reference emulsion (Non-newtonian fluid).