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Use of a mixer-type rheometer for predicting the stability of O/W protein-based emulsions

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ABSTRACT

The present work illustrates the feasibility of performing Oil-in-Water (O/W) emulsions stabilized by different protein concentrates, as well as predicting the likelihood of emulsion destabilization over ageing time just after its preparation. To achieve this objective, four protein sources (rice, crayfish, potato and albumen) and four oil concentrations (450, 550, 650 and 750 g kg^{-1}) were used. The emulsification process was monitored by the use of a mixer-type rheometer. This rheometer was a valuable tool for understanding and controlling the emulsification process through the measurement of the viscosity of the different systems during the emulsification stage.

Results reveal the importance of controlling the emulsification process to optimize the properties of the final emulsion, which is highly influenced by the oil concentration. Then, emulsions were characterized by means of flow properties and droplet size distribution (DSD). Eventually, a relationship was found that relates the rheological properties and the microstructure of the final emulsions during and after emulsification stage. These measurements have been demonstrated to be useful in order to predict the stability of protein-based emulsions.

1. Introduction

An emulsion is a mixture of two immiscible liquids in which one is dispersed in the other in the form of droplets. Common food emulsions are formed by a mixture between oil and water, and are called oil-in-water (O/W) emulsions or water-in-oil emulsions (W/O), depending on the dispersed or continuous phase. The final properties (i.e. stability, texture or droplet size) of an O/W emulsion strongly depend on the specific characteristics of each compound of an emulsion: the dispersed phase (oil), the continuous phase (water) and the interface. Each one of them has its own complexity, which should be analysed to obtain useful information about further emulsion properties. Among them, the interface became of particular interest in these types of kinetically-stabilized systems. The O/W interface of a food is usually stabilized by proteins, low-molecular weight emulsifiers (mainly monoglycerides, phospholipid and esters) or a combination of them (McClements, 2004). Characteristics of the interface depend on the type and concentration of the emulsifier, which tends to be adsorbed at interfacedue to its amphiphilic character. Proteins are widely used as emulsifier in food emulsions, being considered as a functional ingredient in the formation and stabilization of food emulsions and foams (McClements, 2004; Taherian, Fustier, & Ramaswamy, 2006). Proteins are quickly adsorbed at O/W interface of the droplet formed and form a film which protects droplets against destabilization phenomena (Dickinson & McClements, 1995; Foegeding & Davis, 2011; Law & Kennedy, 1999). In recent years, egg yolk has been replaced by alternative protein systems such as vegetable proteins, mainly soybean and wheat, or, even animal proteins systems. Among other alternatives, rice, potato and crayfish protein systems could be mentioned.

Rice industry produces every year a large amount of by-products which involve an undesirable environmental effect. Thus, around 100 million tons of them are produced every year around the world (Li, Liu, Liao, & Yan, 2010). Unfortunately, these by-products are used in low-value-added applications, being mainly incinerated to obtain electricity or used for animal feeding (Njie & Reed, 1995). Another by-product from food industry comes from the potato protein corresponding to the potato skin. Potato protein concentrate from industrial wastes are generally subjected toextreme conditions to increase the protein solubility, as a consequence,

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proteins are extensively denaturated. However, some emulsifying of these potato concentrates have been found (Romero et al., 2011; van Koningsveld, Walstra, Voragen, Kuijpers, van Boekel, & Gruppen, 2006). On the other hand, protein surpluses not only may come from plants but also they may derive from an animal source. For example, proteins form the crayfish *Procambarus clarkii*. It was introduced in Andalusia (southern region of Spain) some years ago and suffered a fast widespread growth, being considered as an invasive species (Kirjavainen & Westman, 1999). Nowadays, a strong local industry produces a big amount of surpluses and wastes. Emulsions have been made from this protein surplus (Felix, Romero, & Guerrero, 2017; Romero, Cordobes, & Guerrero, 2009).

During the emulsification process, the strain and rupture of the droplets are controlled by a local capillary number (Ca), which establishes the relationship between the shear stress and the interfacial tension. Hence, there is a critical value for this relationship that depends on the viscosity ratio of disperse and continuous phases. Above the critical value, shear forces exceed surface tension and the breakup of droplets takes place. However, below this critical value the recoalescence process is more relevant (Janssen & Meijer, 1995).

On the other hand, the stability of an emulsion is the key factor considered for performing an emulsion since these are only kinetically stable. An emulsion is stable when the number, size distribution and spatial distribution of droplets do not change over time. Thus, the destabilization of emulsions mainly depends on the initial size of droplets, the rheology of the continuous phase and the interactions among particles, which are responsible for the flocculation and further coalescence of droplets (Sahin & Sumnu, 2006). Destabilization phenomena are related to the presence of attractive interactions (van der Waals), electrostatic repulsions and steric interactions. Then, if attractive interactions are weak, droplets tend to form a reversible structure which favours the stability. However, if attractive forces are strong the destabilization of emulsions may take place through the droplet flocculation and further coalescence (Tadros, 2013). At equilibrium, proteins adsorbed at O/W are able to form a film which has a double function: On one hand, it favours the electrostatic repulsions. In fact, high values of electrostatic potentials are desired for the stability of this kind of dispersed system (Franco, Guerrero, & Gallegos, 1995). On the other hand, the relatively high film thickness that may act as a mechanic barrier which avoids the droplet coalescence, due to its viscoelastic properties (Tadros, 2013; W. N.; Zhang, Waghmare, Chen, Xu, & Mitra, 2015).

Apart from the colloidal stability, the rheology of emulsions is influenced by several structural parameters, such as interparticle interactions, particle size, shape and polydispersity, continuous phase viscosity, etc. (Martínez, Partal, Muñoz, & Gallegos, 2003). Among them, the nature of the interactions among particles has particular relevance. Moreover, other parameters such as the size and the shape of particles, the polydispersity and rheology of the continuous medium also determine the rheological response significantly (Ma & Barbosa-Cánovas, 1995). The stability of an emulsion can be determined through the use of rheological techniques, since the destabilization phenomena which takes place in an emulsion such as coalescence, creaming, phase inversion or sedimentation provoke changes in the rheological properties of emulsions (Sanchez, Berjano, Guerrero, Brito, & Gallegos, 1998; Tadros, 2013). Rheological measurements are useful because it is possible to relate these properties withthe microstructure of the emulsions, allowing a prediction of emulsion stabilities. Especially interesting are flow measurements in steady and transitory states. Thus, since the first one contributes to describe the real response of emulsions during its transport, the second one reflects the way in which the structural construction or destruction takes place, reflecting also the shear effect (Gallegos, Franco, & Partal, 2004; Guerrero, Partal, Berjano, & Gallegos, 1996; Mezger, 2006). More specifically, the study of the rheological properties during the emulsification stage allows getting knowledge about the shear-induced droplet formation. This characterization at an early stage is of crucial importance to predict the properties and the long-term stability of the final emulsions.

In a previous manuscript, the mixer-type rheometer was used as a tool to evaluate the influence of agitation speed, oil and protein concentrations as well as pH on the properties of egg albumen-based emulsions over emulsification (Romero, Perez-Puyana, Marchal, Choplin, & Guerrero, 2017). The aim of this study was to compare the use of four different proteins (rice, crayfish, potato and albumen) in mayonnaise type O/W emulsion stabilization at four different oil concentrations (450, 550, 650 and 750 g oil per kg emulsion) over and after processing by a mixer-type rheometer, as well as predicting the likelihood of emulsion destabilization over ageing time just after its preparation. Therefore, characterization of the emulsions, particularly its viscosity and particle size distribution, was carried out to accomplish this objective.

2. Materials and methods

2.1. Materials

Different protein systems were used. The rice protein concentrate, from rice husks, was provided by Remy Industries (Leuven-Wijgmaal, Belgium), the crayfish flour was obtained from ALFOCAN S.A. (Isla Mayor, Seville, Spain), potato protein isolate was supplied by Protastar (Reus, Barcelona, Spain) and blbumen protein isolate was delivered by Proanda (Barcelona, Spain). Table 1 shows the composition for each protein concentrate system supplied. Sunflower oil was purchased in a local market and used without further purification. In addition, more information about molecular weight distribution, isolelectric point and protein solubility as a function of pH values as well as interfacial properties of these protein systems can be found in the literature (Felix, Martin-Alfonso, Romero, & Guerrero, 2014; Romero et al., 2012; Romero, Beaumal, et al., 2011; Romero, Cordobes, Guerrero, & Cecilia Puppo, 2011).

2.2. Emulsification process

Emulsions were prepared in a mixer-type rheometer. This device consists of a cylindrical vessel equipped with a double helical ribbon impeller installed in a RS150 controlled stress rheometer, as described by (Nzihou, Bournonville, Marchal, & Choplin, 2016). Different O/W protein-based emulsions were prepared by means

Table 1
Composition of different protein type systems: Rice, Crayfish, Potato and Albumen.

Protein System	Protein ($g \cdot kg^{-1}$)	Carbohydrates ($g \cdot kg^{-1}$)	Ash ($g \cdot kg^{-1}$)	Lipids ($g \cdot kg^{-1}$)	Moisture ($g \cdot kg^{-1}$)
Rice	782 ± 12	64 ± 3	52 ± 1	24 ± 3	78 ± 4
Crayfish	647 ± 12	2 ± 1	134 ± 2	183 ± 8	34 ± 3
Potato	801 ± 23	59 ± 6	8 ± 1	31 ± 4	101 ± 2
Albumen	730 ± 11	4 ± 1	60 ± 3	130 ± 5	76 ± 2