Food Hydrocolloids 25 (2011) 1521–1529

Contents lists available at ScienceDirect

Food Hydrocolloids

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

Oil-in-water emulsions stabilized by chitin nanocrystal particles

Maria V. Tzoumaki [a], Thomas Moschakis [a], Vassilios Kiosseoglou [b], Costas G. Biliaderis [a,*]

[a] *Department of Food Science and Technology, School of Agriculture, P.O. Box 235, Aristotle University of Thessaloniki, GR-54124 Thessaloniki, Greece*
[b] *Laboratory of Food Chemistry and Technology, Department of Chemistry, Aristotle University of Thessaloniki, GR-54124 Thessaloniki, Greece*

ARTICLE INFO

Article history:
Received 25 November 2010
Accepted 8 February 2011

Keywords:
Pickering emulsions
Oil-in-water emulsions
Chitin nanocrystals
Rod-like particles
Creaming
Rheology
Microstructure

ABSTRACT

The aim of the present study was to investigate the oil-in-water emulsion stabilizing ability of chitin nanocrystals (colloidal rod-like particles) and the factors that may influence the properties of such systems. Chitin nanocrystal aqueous dispersions were prepared by acid hydrolysis of crude chitin from crab shells and oil-in-water emulsions were generated by homogenizing appropriate quantities of a chitin nanocrystal stock aqueous dispersion with corn oil, using an ultra-sonic homogenizer. The resulting emulsions were visually evaluated for their creaming behaviour upon storage. Additionally, the samples were studied with static light scattering, small deformation oscillatory rheometry and optical microscopy, under different conditions of nanocrystal concentration, ionic strength, pH and temperature. The chitin nanocrystals were proven quite effective in stabilizing o/w emulsions against coalescence, over a period of one month, as evidenced by static light experiments and microscopy, and this could be attributed to the adsorption of the nanocrystals at the oil–water interface. The rheological data provided evidence for network formation in the emulsions with increasing chitin nanocrystal concentration. Such a gel-like behaviour was attributed to an inter-droplet network structure and the formation of a chitin nanocrystal network in the continuous phase. The stability of the emulsions to creaming increased with an increase in nanocrystal concentration. Finally, by raising the temperature (20–74 °C), NaCl concentration (up to 200 mM) or pH (from 3.0 to 6.7) there was an enhancement of the emulsion elastic character and creaming stability.

1. Introduction

Emulsions are of great practical interest because of their extensive occurrence in food, cosmetics and pharmaceutical industries (Vignati, Piazza, & Lockhart, 2003). Emulsion preparation and stabilization can conventionally be achieved by prolonged mechanical agitation and addition of surfactants or other surface active polymers (Ashby & Binks, 2000; Vignati et al., 2003). Early works have shown that emulsion stability does not necessarily require amphiphilic surfactants to reduce the interfacial tension, but can also be efficiently achieved by dispersed solid particles of colloidal dimensions (Pickering, 1907; Ramsden, 1904). The emulsions stabilized by such particles are usually referred as Pickering emulsions.

The conventional explanation for emulsion stabilization by solid particles is their accumulation at the oil–water interface in the form of a densely packed layer, which may prevent droplet flocculation and coalescence by a steric mechanism (Binks & Horozov, 2006; Dickinson, 2006, 2010). The extent of steric barrier depends on how difficult it is to remove particles from the interface, and is greater when most of the particles' surfaces lay on the outer side of the oil droplets (Dickinson, 2010). Therefore, the contact angle θ made by the stabilizing colloidal particles at the water–oil contact line, determines the particle location at the interface and the nature of the emulsion. Contact angles less that 90°, imply the hydrophilic nature of the colloidal particles that gives rise to o/w emulsions, whereas contact angles greater than 90° imply the hydrophobic nature of the particles that favours w/o emulsion formation (Lagaly, Reese, & Abend, 1999; Vignati et al., 2003). Moreover, the energy of desorption per particle is related to the contact angle θ and as long as θ is not close to 0° or 180°, it is predicted to be of the order of several thousand kT (Aveyard, Binks, & Clint, 2003; Dickinson, 2010; Yusoff & Murray, 2011). This denotes that once the particles are at the interface, they are effectively and irreversibly adsorbed. Hence, one of the most striking features of the particle-stabilized emulsions is that, in most of the cases, they are extremely stable to coalescence even when the droplets are quite large (Binks, Dyab, & Fletcher, 2007; Dickinson, 2010).

In addition to the particle layer formation around the droplets, some other ordering mechanisms responsible for the prevention of

---

* Corresponding author. Tel./fax: +30 2310 991797.
E-mail address: biliader@agro.auth.gr (C.G. Biliaderis).

0268-005X/$ – see front matter © 2011 Elsevier Ltd. All rights reserved.
doi:10.1016/j.foodhyd.2011.02.008

droplet coalescence have been proposed for Pickering emulsions. One of these is aggregation of the particles, where the steric particle-based barrier is not a simple bilayer or monolayer which is densely packed, but a network of particles, adsorbed at the oil–water interface, with the whole aggregated structure held together by attractive inter-particle forces (Denkov, & Lips, 2008; Gautier et al., 2007; Tcholakova). The properties of Pickering emulsions are usually determined by particle size (Binks & Lumsdon, 2001), particle wettability (Binks & Clint, 2002), particle concentration (Binks, Philip, & Rodrigues, 2005), oil/water ratio (Binks & Lumsdon, 2001; Binks & Whitby, 2004), pH (Midmore, 1998), salt concentration (Whitby, Fornasiero, & Ralston, 2009), and solvent type (Tambe & Sharma, 1994a).

A variety of particles of different size, shape, and surface chemistry have been used to stabilize emulsions including hydrophobic silicas (Binks & Lumsdon, 2001; Binks & Whitby, 2004; Midmore, 1998), clays (Ashby & Binks, 2000), carbon nanotubes (Shen & Resasco, 2009), and latexes (Ashby, Binks, & Paunov, 2004; Binks & Lumsdon, 2001). Although there is a lot of research conducted on particle-stabilized emulsions, fairly few of them are directly related to foods (Dickinson, 2010). This is probably due to the different type of particles that are used, or the modifications applied to them, which are not allowed in foods. On the other hand, food systems frequently include particle-type material that may play a role to the stabilization of emulsions (Dickinson, 2010). Some examples of Pickering-type food emulsions are homogenized and reconstituted milks (o/w emulsions stabilized by casein micelles), margarines and fat spreads (i.e. w/o emulsions stabilized by triglyceride crystals) (Dickinson, 2006; Hunter, Pugh, Franks, & Jameson, 2008) Moreover, some potentially food-compatible particulate materials that have been used in emulsion stabilization include plant or bacterial cellulose fibres (Andresen & Stenius, 2007; Paunov et al., 2007; Wege, Kim, Paunov, Zhong, & Velev, 2008), and lately modified starch granules (Yusoff & Murray, 2011).

Natural biopolymers, like polysaccharides, can be an attractive source of particulate material for potential food use. One example is chitin, which is a structural biopolymer found in shellfish, insects, and microorganisms and is the second most abundant polysaccharide in nature. It has been previously reported that acid-hydrolyzed chitin preparations spontaneously disperse into rod-like crystalline particles of nanodimensions (Belamie, Davidson, & Giraud-Guille, 2004; Marchessault, Morehead, & Walter, 1959; Revol & Marchessault, 1993). These chitin nanocrystals possess positive charges at their surface due to protonation of the amino groups (Li, Revol, Naranjo, & Marchessault, 1996). It has also been shown that such colloidal dispersions of acid-degraded chitin can undergo an isotropic–anisotropic nematic transition when their concentration is increased (Marchessault et al., 1959; Revol & Marchessault, 1993; Belamie et al., 2004). Regarding chitin nanocrystal (ChN) aqueous dispersions, it has been reported in our previous works, that they shift towards a nematic gel-like behaviour with increasing solid particle concentration, ionic strength, pH and temperature (Tzoumaki, Moschakis, & Biliaderis, 2010), as well as by adding whey proteins (Tzoumaki, Moschakis, & Biliaderis, 2011). The ChN dimensions were previously measured by TEM (Tzoumaki et al., 2010) and found to be on average 240 nm in length and 18 nm in diameter. There are very few studies on Pickering emulsions stabilized by particles with different shape other that spherical. Some examples include laponite platelets-stabilized emulsions (Ashby & Binks, 2000), and calcium carbonate needle-like particles (Paunov et al., 2007). Moreover, it has been found that the particle shape has a strong impact on the stability and properties of the emulsions (Madivala, Vandebril, Fransaer, & Vermant, 2009); i.e., emulsions that cannot be stabilized by spherical particles yield very stable emulsions when particles of the same surface chemistry and size range, but with a sufficiently large aspect ratio, are used, even at low volume fractions. Additionally, surface shear rheology has been used to demonstrate that the shape anisotropy leads to monolayers with pronounced viscoelastic properties (Madivala et al., 2009).

The aim of the present work was to investigate the preparation and characterization of corn oil-in-water (o/w) emulsions stabilized by chitin nanocrystals and the factors that may influence the properties of such systems, like chitin nanocrystal concentration, ionic environment, pH and temperature. The emulsion characterization was carried out by visual observations, static light scattering experiments, rheometry and optical microscopy in an attempt to understand the underlying stabilization mechanism(s).

2. Materials and methods

2.1. Materials

Crude chitin from crab shells was obtained from Sigma Chemicals (St Louis, MO). Hydrochloric acid (concentrated 37% v/v), sodium acetate, glacial acetic acid, potassium hydroxide, sodium chlorite and sodium chloride were all of reagent grade and purchased from Sigma Chemicals (St Louis, MO). Corn oil was obtained from a local supermarket and used without further purification. Double distilled water was used in all the experiments.

2.2. Chitin nanocrystals preparation

Aqueous stock dispersions of chitin nanocrystals (ChN) were prepared by acid hydrolysis (3 N HCl, 95 °C, 90 min) of the original raw material of crude chitin from crab shells. Detailed information on bleaching (with sodium chlorite) and acid hydrolysis are given elsewhere (Tzoumaki et al., 2010). The solid chitin content of the stock dispersion was determined gravimetrically by drying the samples at 50 °C until a constant weight was obtained; the total solids content of the stock dispersion was approximately 2.7% w/w. The final pH of the stock ChN dispersion was adjusted to 3.0 with 1 N HCl.

2.3. Emulsion preparation

An oil-in-water emulsion was prepared by mixing appropriate quantities of ChN stock dispersion, corn oil and an aqueous solution adjusted to pH 3.0, using an ultra-sonic homogenizer (Sonics & Materials, Inc. Danbury, Connecticut, USA, Power 50/60 Hz) for 2 min with 20 s intervals, to avoid overheating of the samples. The corn oil concentration was always adjusted to 10% w/w, while the ChN concentration varied; all the concentrations refer to the whole emulsion and not just to the aqueous phase. A series of emulsions were prepared by adjusting them to different pH and ionic strength values using HCl (1 N) and NaCl solutions, respectively.

2.4. Visual assessment

Freshly prepared emulsions were poured into 5 ml glass tubes (height 75 mm, diameter 9 mm) after preparation. The tubes were then inverted carefully several times to ensure thorough mixing. Subsequently, the tubes were sealed to prevent evaporation. The emulsion samples were stored quiescently at ambient temperature and the movement of any creaming boundaries was followed with time.

2.5. Microscopy

Optical micrographs of the ChN-stabilized o/w emulsions were captured by an Olympus BX 51 optical microscope fitted with a digital camera (Olympus, DP 50). The emulsion samples were