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Properties and stability of oil-in-water emulsions stabilized by microfibrillated cellulose from mangosteen rind

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ABSTRACT

The influence of concentration of microfibrillated cellulose (MFC) extracted from mangosteen (*Garcinia mangostana* L.) rind on the properties and stability of 10% w/w soybean oil-in-water (o/w) Pickering emulsions (pH ≈ 7.0) was examined. The MFC concentration in the aqueous phase was varied from 0.05 to 0.70% w/w. The mean droplet size and the color intensity of the emulsions increased with increasing MFC concentration. Microscopic observations revealed that the MFC particles mainly adsorbed at the oil-water interface of the emulsion droplets, whereas the amount of excess non-adsorbing MFC particles present in the continuous aqueous phase increased with increasing MFC concentration. The rheological data provided evidence for network formation in the emulsions with increasing MFC concentration. Such a gel-like behavior was attributed to an inter-droplet network structure and the formation of an MFC network in the continuous phase. All the emulsions were stable to coalescence for a period of 80 days whatever the MFC concentration but the stability to creaming decreased progressively with decreasing MFC concentration. These results have important implication for the rational design and production of particle-stabilized food emulsions.

1. Introduction

A large number of emulsion-based products are of great interest because they play an important role in food, cosmetics, and pharmaceutical industries. An emulsion is a dispersed system that consists of two or more completely or partially immiscible liquids where one of the liquids dispersed as small spherical droplets in the other (McClements, 2005; Zarena, Bhattacharya, & Kadimi, 2012). The emulsions can be formed and stabilized not only by surface-active compounds, e.g. surfactants or proteins, but also by solid particles to form the so-called 'Pickering emulsions' after the original work of Pickering (1907). The mechanism of solid particles stabilized emulsion is the effective and irreversible adsorption of dispersed particles at the oil-water interface to form mechanical (steric) barriers around the emulsion droplets, which prevents their coalescence (Chevalier & Bolzinger, 2013; Dickinson, 2010, 2012). Several characteristics of the solid particles such as particle size (Binks & Lumsdon, 2001), particle shape (Kalashnikova, Bizot, Bertoncini, Cathala, & Capron, 2013; Madivala, Vandebril, Fransaer, & Vermant, 2009), particle wettability (Kalashnikova, Bizot, Cathala, & Capron, 2012; Xhanari, Syverud, & Stenius, 2011), particle concentration (Frelichowska, Bolzinger, & Chevalier, 2010; Kalashnikova, Bizot, Cathala, & Capron, 2011), and particle interactions and assemblies (Lee et al., 2014; Wongkongkatep et al., 2012) have been reported to play an important role in the properties and stability of the particle-stabilized emulsions. It is generally known that the smaller the solid particle, the higher aspect ratio, and the intermediate wettability, the higher the emulsifying properties of the particle. At relatively low particle concentrations, the emulsion droplet size decreases with increasing particle concentration because more solid particles are available to stabilize smaller oil droplets. On the contrary, at higher particle concentrations, an increase in droplet size may occur due to the higher viscosity of the continuous phase that may reduce the efficiency of emulsification process. The emulsion stability is also enhanced by the interactions of solid particles at the droplet interfaces.

Research efforts are being focused on the production of different types of nanoparticles and microparticles, varying from inorganic to organic, that are not only effective to stabilize emulsions, but also acceptable for use in food products (Dickinson, 2010, 2012). Natural

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biopolymers, like polysaccharides, for examples, hydrophobically modified starch granules (Timgren, Rayner, Dejmek, Marku, & Sjöö, 2013; Yusoff & Murray, 2011), chitin nanocrystals (Tzoumaki, Moschakis, Kiosseoglou, & Biliaderis, 2011), and cellulose nanocrystals (Kalashnikova et al., 2011, 2012, 2013) are becoming an interesting source of particulate material for food use.

Cellulose is the most abundant biopolymers on earth and is an excellent candidate for interfacial stabilization because of its renewability, sustainability, biodegradability, and nontoxicity (Kalashnikova et al., 2011, 2013). Cellulose is a linear homobiopolymer consisting of glucan chains with repeating β-(1 → 4)-D-glucopyranose units. These chains form parallel bundles, the microfibrils, which again aggregate to form cellulose fiber. The isolation of cellulose fibril aggregates using a homogenization process has first been described by Turbak, Snyder, and Sandberg (1983). The resulting cellulose fibers are moderately degraded and opened into their substructural fibrils and microfibrils, which is called microfibrillated cellulose (MFC). MFCs are generally produced from cellulosic plant materials such as wood, agricultural crops and by-products, which are the most abundant resources and are underutilized sources of cellulose.

Mangosteen fruits are generally considered to be one of the finest flavored fruits which earn the popular title of 'Queen of Fruits'. The economic importance of the mangosteen, both for domestic use and export, is increasing as domestic and overseas demand increases. Thailand is the largest producer as well as exporter of mangosteen. In 2012, 200,000 tons of fruits were harvested and 150,000 tons were exported (Office of Agricultural Economics, Ministry of Agriculture and Cooperatives, Thailand, 2014). Fruit weights vary from 75 to 150 g. The edible fruit pulp or aril is white, soft, and juicy with a sweet, slightly acid taste and a pleasant aroma. The pericarp, rind or skin of the fruit is dark purple to red-purple, smooth, thick, and tough (Yaacob & Tindall, 1995). Mangosteen rind, which is about two thirds of the whole fruit weight, is usually disposed as agricultural waste (Zarena et al., 2012). These wastes are rich in cellulose and have been used for the production of MFC (Winuprasith & Suphantharika, 2013).

MFCs have many interesting properties, such as an extremely large specific surface area, very high longitudinal aspect ratios, high strength and stiffness, low density, and ability to form a stable aqueous suspension, providing an opportunity for multiple uses as dietary fibers, thickeners, emulsifiers or additives in food products (Habibi, Mahrouz, & Vignon, 2009; Turbak et al., 1983). Due to the hydrophilic nature of cellulose, MFCs are better wet by water than oil, and, thus, tend to stabilize oil-in-water (o/w) emulsions (Xhanari, Syverud, & Stenius, 2011).

In a previous study, we have examined the influence of preparation conditions, i.e. the number of homogenization passes, on the characteristics and functional properties of MFC from mangosteen rind (Winuprasith & Suphantharika, 2013). These MFCs were characterized in terms of chemical composition, crystallinity, degree of polymerization, and rheological properties using chemical analyses, x-ray powder diffraction (XRD), viscosimetric method, and rheometry, respectively. Their functional properties were evaluated in terms of emulsion stabilizing properties. This study has shown that the o/w emulsions stabilized by MFC obtained with higher number of homogenization passes had smaller oil droplets, stronger three-dimensional network structures, and more stable to creaming than those stabilized by MFC produced at lower number of homogenization passes.

In most of the studies performed on emulsions stabilized by cellulose nanofibers, it was found that structural aspects, such as average diameter and length (calculated in terms of aspect ratio = length/diameter), of the cellulose nanofibers significantly affect the properties of resultant emulsions (Kalashnikova et al., 2013). Generally, the nanofiber dimensions are determined using a combination of microscopic techniques with image analysis. However, in the case of MFCs, a very high aspect ratio (Pääkkö et al., 2007) prevents precise estimation of their length due to entanglements and difficulties in identifying both ends of the individual MFCs (Varanasi, He, & Batchelor, 2013). Due to this shortcoming, alternative methods such as gel point measurements of the MFC suspension have been proposed (Varanasi et al., 2013), which were not carried out in this work. In this study, we investigated the influence of MFC concentration on the physical and rheological properties as well as stability to either creaming or coalescence of the o/w MFC-stabilized Pickering emulsions.

2. Materials and methods

2.1. Materials

Dried mangosteen rind (*Garcinia mangostana* L.), a by-product of mangosteen-canning process, was supplied by a local manufacturer (Chanthaburi, Thailand). Sodium hydroxide (NaOH) and phosphoric acid (H_3PO_4) were obtained from Mallinckrodt Baker, Inc. (Phillipsburg, NJ, USA). Hydrogen peroxide (H_2O_2) and Congo red dye (C.I. 22120) were obtained from Merck KGaA (Darmstadt, Germany). Nile red dye and sodium azide (NaN_3) were obtained from Sigma Chemical Company (St Louis, MO, USA). All reagents were of analytical grade and distilled water was used for preparation of all solution and emulsion. Soybean oil was purchased from a local supermarket and used without further purification.

2.2. Preparation of microfibrillated cellulose

Microfibrillated cellulose (MFC) was prepared according to a previously described protocol (Winuprasith & Suphantharika, 2013). Briefly, dried mangosteen rind was ground to pass through a 100 mesh sieve. The resulting mangosteen rind powder was extracted for cellulose using hot (90 °C) aqueous NaOH solution at pH 12, washed, neutralized, and then bleached using hot H_2O_2 solution. The yellow-brown, water swollen purified cellulose was collected by filtration. The purified cellulose was used for the preparation of MFC by re-dispersing in distilled water at a concentration of 1% w/w and then passing through a high pressure homogenizer (type Panda, Niro-Soavi S.p.A, Parma, Italy) at a pressure of 500 bar for 20 passes at room temperature (25 °C). The resulting material was yellow-brown gel-like aqueous matter, having an MFC concentration of 1% w/w and exhibiting neither flocculate nor sediment when diluted with water.

2.3. Preparation of MFC-stabilized emulsions

MFC aqueous suspensions were prepared at concentrations of 0.05, 0.10, 0.30, 0.50, and 0.70% w/w by dilution of the stock 1% w/w MFC suspension using distilled water. The MFC concentration reported in this paper refer to the aqueous phase and not to the whole emulsion. MFC-stabilized oil-in-water (o/w) emulsions (500 g each) were prepared by blending 10% w/w soybean oil and 90% w/w MFC aqueous suspensions together using a rotor-stator (model Ultra Turrax T18, IKA® Works, Inc., Wilmington, NC, USA) at 11,000 rpm for 1 min and followed by 15,000 rpm for another 4 min. These coarse emulsions were then passed through a two-stage high-pressure homogenizer (type Panda, Niro-Soavi S.p.A, Parma, Italy) at pressures of 500/50 bar for the first/second stages homogenizing valves, respectively for 3 passes at room temperature. NaN_3 (0.01% w/w) was used as a preservative. The samples were stored at room temperature for at least 1 day before being analyzed.