



Pickering oil-in-water emulsions stabilized by carboxylated cellulose nanocrystals – Effect of the pH

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ABSTRACT

Carboxylated cellulose nanocrystals (cCNC) were prepared by oxidation of microcrystalline cellulose with ammonium persulfate and characterized by AFM. Zeta potential was measured at different pH and ionic strength, in presence of mono- and divalent cations. With a length ranging from 50 to 450 nm and a thickness varying between 20 and 60 nm, the cCNC had a surface charge that appeared to be more sensitive to the presence of divalent cations and exhibited a strong pH dependence. The nanocrystals were capable of forming stable oil-in-water emulsions at three different pH of 2, 4 and 7 with a triglyceride oil. The size of emulsion droplets was dependent on oil and cCNC contents. Emulsification was, however, mainly influenced by the pH of the continuous phase, which can be related to reduction of charge on the cCNC surface with decreasing pH. Responsiveness of emulsions towards pH changes was not as dominant as expected, and lowering of pH did not trigger the release of oil from droplets. This can be explained by the strong adsorption of the cCNC, relatively polar triglyceride oil and the limited possibility to induce desorption of nanocrystals from oil surface.

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1. Introduction

Over the past decades, an increasing interest in the development and application of particle-stabilized emulsions has appeared (Aveyard, Binks, & Clint, 2003; Binks, 2002), driven by the effort to replace, at least partially, synthetic surfactants known for their topical toxicity (Lémery et al., 2015). In the field of food science, Pickering emulsions have been around since long, and various types of synthetic particles, whether organic or inorganic, have been used as emulsion stabilizers (Lam, Velikov, & Velez, 2014; Wu & Ma, 2016; Xiao, Li, & Huang, 2016). The call for using environmentally sustainable as well as neutral resources has oriented the interest towards materials of natural origin. Among such type of

materials cellulose particles have attracted a great interest, especially for food related applications. (Chen et al., 2018; Mikulcová, Bordes, & Kašpárková, 2016; Wang et al., 2016; Winuprasith & Suphantharika, 2013; Yan et al., 2017). There is a variety of suitable types of cellulose-based particles for the stabilization of emulsions, and cellulose nanocrystals (CNC) have proven to be very efficient in stabilizing interfaces (Capron, Rojas, & Bordes, 2017). CNC is obtained from a top-down preparation route that allows the removal of the amorphous part of cellulose fibres to extract the more crystalline portions (Habibi, Lucia, & Rojas, 2010; Peng, Dhar, Liu, & Tam, 2011; Zhang et al., 2013). The removal of the amorphous part can be carried out by several procedures, all of which significantly influence the surface properties and the applicability of the final CNC. The more common methods employ treatments of cellulose containing materials with acids, enzymes, oxidation agents, mechanical stress or a combination of them (Cao, Dong, & Li, 2007; Filson, Dawson-Andoh, & Schwegler-Berry, 2009; Jonobi et al., 2015; Montanari, Roumani, Heux, & Vignon, 2005; Revol, Bradford, Giasson, Marchessault, & Gray, 1992; Sacui et al., 2014). In contrast to the well-established hydrolysis of cellulose by sulfuric acid that

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gives stable colloidal suspensions of cellulose nanocrystals which exhibit a low pH dependence (Irina Kalashnikova, Bizot, Cathala, & Capron, 2011; Wang et al., 2016), alternative routes have been developed for preparing pH responsive CNC. For instance, by treating a nanocellulose with the so-called TEMPO oxidant several groups obtained highly crystalline CNCs bearing carboxylic groups on the surface, referred to as carboxylated cellulose nanocrystals (cCNC) (Isogai, Saito, & Fukuzumi, 2011; Jia et al., 2016; Shimizu, Fukuzumi, Saito, & Isogai, 2013). More recently, Leung et al. (2011) reported an original and simple method for the direct preparation of cCNC by employing a strong oxidizing agent, ammonium persulfate (APS). This procedure could be used for the processing of variety of native plant fibres and other cellulose sources.

Whereas several studies report on the application of bare nanocellulose for stabilizing oil-in-water emulsions (see for instance the pioneering work by Irina Kalashnikova et al., 2011; I. Kalashnikova, Bizot, Cathala, & Capron, 2012; Wang et al., 2016; that has been followed by others Hu et al., 2015a; Hu et al., 2015b) or after hydrophobization, water-in-oil emulsions (Lee, Blaker, Heng, Murakami, & Bismarck, 2014; Saidane, Perrin, Cherhal, Guellec, & Capron, 2016), much less work has been dedicated to the emulsification performances of cCNC, especially in relation to the pH responsiveness. In 2014, Wen et al. studied the emulsification of D-limonene by carboxylated cellulose nanocrystals prepared via APS treatment of corn cob cellulose. They obtained system with double responsiveness, both towards temperature and pH; stability of the emulsions was improved by increased temperature, whilst it was reduced at low pH or high salt concentration due to electrostatic screening of the negatively charged cCNC particles. However, in this unique example no systematic study on the pH dependent behaviour of cCNC stabilized emulsions was reported.

The present work, therefore, focuses on the formulation of cCNC stabilized Pickering emulsions prepared at three different pH, and on the characterization of their behaviour in terms of particle size, zeta potential and phase behaviour. The oil phase of the emulsions was triglyceride oil, which is commonly used as a neutral carrier for various lipophilic bioactive substances. The employed carboxylated nanocrystalline cellulose was prepared via a one-step oxidation procedure by APS. The nanocrystals were characterized using atomic force microscopy (AFM) and dynamic light scattering (DLS). Behaviour of cCNC under different pH and ionic strength was studied by zeta potential measurements.

2. Materials and methods

2.1. Materials

Microcrystalline cellulose Avicel® PH-101 and ammonium persulfate both supplied by Sigma Aldrich (Germany) were used for the preparation of cellulose nanocrystals. The nanocrystals were utilized for the preparation of emulsions containing tricaprylin/tricaprin oil (Tegosoft®CT, Evonik Industries AG, Germany). Water was purified by reverse osmosis (0.06 µS/m). Tegosoft composition, according to Ph.Eur. was as follows: caproic acid ≤2%, caprylic acid 50–65%, capric acid 30–45%, lauric acid ≤2% and myristic acid ≤1%. Hydrochloric acid, sodium hydroxide, calcium chloride, sodium chloride (IPL Petr Lukeš, Czech Republic) were used without purification.

2.2. Preparation of cellulose nanocrystals

Cellulose nanocrystals were prepared by adapting a procedure inspired by Leung et al. (2011). To 10 g of microcrystalline cellulose was added 1 L of 1 M APS solution. The suspension was first heated

at 50 °C for 15 min and temperature was then increased to 70 °C. The stirring of the solution was kept at this temperature for 24 h. The suspension was centrifuged (7000 rpm) for 10 min using Superspeed Centrifuge Sorvall Lynx 4000 (Thermo Scientific, USA). After each centrifugation, supernatant was decanted and replaced with purified water. The centrifugation/washing cycle was repeated until conductivity of suspension reached 3 µS/cm. The suspension was then sonicated for 30 min at an amplitude of 40% using a UP400S sonicator (Heielscher, Germany) after adjusting the pH to 7 with NaOH (~1M). Finally, the concentration of cCNC dispersion was adjusted to 2 % wt by removing the water with a rotary evaporator.

2.3. Characterization of nanocrystals

Atomic force microscope (AFM) PeakForce TUNA module on Dimension ICON (Bruker Corporation, USA) was utilized for the characterization of the cellulose nanocrystals. The measurements were conducted at normal RH and room temperature in semi-contact mode. A silicon nitride probe (Bruker Corporation, USA) with a spring constant of 5 N/m and resonant frequency of 150 ± 50 kHz was employed. The image was recorded at a scanning rate of 0.5 Hz.

Particle size, particle size distribution, polydispersity index (PDI) and zeta potential were determined by dynamic light scattering (DLS) carried out on a Zetasizer Nano ZS90 instrument (Malvern Instruments, Malvern, UK). The analyses were carried out on samples diluted in water at a scattering angle of 90° and temperature of 25 °C. Prior to the measurements, the suspension was filtered with a hydrophilic 800 nm syringe filter (Sartorius). Zeta potential of cCNC particles was measured over a pH range of 2–10. The cCNC suspensions were diluted (0.35%) in pH-adjusted water containing 1 mM NaCl as a background electrolyte. Correspondingly, zeta potential at pH of 6.9 at different ionic strengths of dispersion media was determined using series of NaCl and CaCl₂ solutions with concentrations ranging from 0 to 100 and 0–10 mM, respectively. The ionic strength was calculated using equation $I = \frac{1}{2} \sum c_i z_i^2$, where c_i represents the molar concentration of the ion and z_i is the charge number of that ion. All sizing and zeta potential measurements are reported as means and standard deviations was calculated on the basis of at least three repeated measurements.

2.4. Stability of oil under emulsification

In order to verify the stability of the triglyceride oil during the emulsification, acid value of the oil was determined prior and after 1 and 10 min sonication according to a standard procedure described elsewhere (AOCS & Firestone, 2011).

2.5. Preparation of emulsions

Prior to emulsification, the cCNC suspension was sonicated for 5 min using a UP400S sonicator (Heielscher, Germany) in order to disintegrate agglomerates possibly formed during storage. Individual components of each of the emulsion (oil, water and cCNC) were, in pre-calculated amounts, weighed directly into the glass vial. The aqueous phase containing cCNC was left either native (pH of 7) or adjusted using HCl to pH of 4 and 2. Oil to water (O/W) ratios of 10/90, 20/80, 30/70 and 40/60 were used. Four different concentrations of cCNC of 0.01, 0.05, 0.1, and 0.3 wt % were applied. The cellulose mass content refers to its content in the total emulsion. Emulsifications were carried out using sonication (UP400S sonicator), (Heielscher, Germany) for 1 min at 100% amplitude. During the preparation, the samples were cooled down with an ice bath.

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