Chemical Engineering Journal 288 (2016) 312–320

Contents lists available at ScienceDirect

Chemical Engineering Journal

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

Nanoparticle emulsifiers based on bifunctionalized cellulose nanocrystals as marine diesel oil–water emulsion stabilizers

Jonna Ojala, Juho Antti Sirviö, Henrikki Liimatainen *

Fiber and Particle Engineering, P.O. Box 4300, FI-90014 University of Oulu, Finland

HIGHLIGHTS

- Bifunctionalized cellulose nanocrystals (*But*-CNCs) were used to stabilize o/w emulsion.
- *But*-CNCs reduced the oil-droplet size in emulsions and acted as a stabilizer.
- The background salt concentration had only a slight effect on *But*-CNC performance.
- *But*-CNCs can potentially act as "green" oil spill response agents.

ARTICLE INFO

Article history:
Received 16 July 2015
Received in revised form 28 October 2015
Accepted 31 October 2015
Available online 11 December 2015

Keywords:
Dispersing agent
Nanocellulose
Nanoparticle
Oil spill
O/w emulsion

ABSTRACT

The preparation and properties of marine diesel oil-in-water (o/w) emulsion stabilized by bifunctionalized cellulose nanocrystals (*But*-CNCs) were investigated. Bifunctional *But*-CNCs containing both carboxylic and *n*-butylamino groups were obtained using partial, sequential periodate–chlorite oxidation and reductive amination, followed by a homogenization treatment to liberate individualized nanocrystals with amphiphilic characteristics. The fabricated *But*-CNC suspensions were optically transparent, and the nanocrystals that were isolated were rod-like, with lengths ranging between 35 and 120 nm and with lateral dimensions varying from 2 to 4 nm. Bifunctionalized CNCs at low concentrations (up to 0.45 wt%) were investigated as possible surface-active stabilizers in o/w emulsions. In particular, their ability to enhance the emulsification of marine diesel oil in an aqueous environment was addressed in order to evaluate their potential to be used as "green" oil spill response agents. *But*-CNCs at 0.1 wt% concentration in dispersion reduced the oil particle size from 50 μm to 9–16 μm, and the stability against coalescence was improved in emulsions where bifunctionalized CNCs were used compared to plain o/w emulsion.

In addition, the influence of *But*-CNC dosage and emulsion salinity (0–5% NaCl by weight) was investigated. The background salt concentration only had a minor effect on droplet size, and the stabilization effect was still apparent, with high electrolyte concentration. These results demonstrate the potential of bifunctionalized cellulose (with surface-active groups attached) to act as a nanoparticle emulsifier in oil–water emulsions, thus enabling its utilization in oil-destruction activities.

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1. Introduction

As a renewable and abundant raw material, plant celluloses have become an attractive resource in the development of novel "green" materials and chemicals for the emerging bio-based economy. In addition to the utilization of celluloses in the form of fibers, researchers have paid a great deal of attention to the fabrication and exploitation of micro- and nano-sized cellulose constitutes, such as cellulose nanocrystals (CNCs) and cellulose nanofibrils, in multiple applications [1–7]. CNCs possess many advantages like unique optical properties, and higher strength properties such as stiffness and modulus [8]. A typical individual cellulose crystal from a wood source is approximately 3–5 nm in diameter, with a length of 200 nm or less [3]. Depending on the cellulose source, the aspect ratios (length to width [L/w]) of CNCs range from 10 to 100 [1]. The presence of several hydroxyl groups on the surfaces of CNCs makes them inherently hydrophilic, and enhances their interaction with water [9,10].

One traditional way to produce CNCs (also known as nanocrystalline cellulose or cellulose "nanowhiskers") is to conduct strong acid hydrolysis, which dissolves the amorphous regions from the

* Corresponding author. Tel.: +358 505659711.
E-mail address: Henrikki.Liimatainen@oulu.fi (H. Liimatainen).

http://dx.doi.org/10.1016/j.cej.2015.10.113
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cellulose structure and yields pure, nano-sized crystalline cellulose particulates [1]. Today, other chemical, enzymatic, or mechanical methods (or a combination of these methods) are also used in CNC fabrication [3,9]. The first non-acidic treatment to produce CNCs was the APS (ammoniumpersulfate extraction) method [11], although researchers have recently developed another acid-free oxidative pre-treatment to produce nanocrystals with tuned surface properties [9,10]. In this approach, the surface modifications can be conducted during the pre-treatment step before liberating the individual CNCs, which reduces the need for difficult and time-consuming post-treatments [10].

Several different chemicals are used to promote the dispersion and stabilization of o/w emulsions. These dispersants or emulsifying agents (which are typically soluble compounds with amphiphilic characteristics) minimize interfacial energy, thus enhancing emulsions' long-term stability [12]. Dispersants can also be used in the form of nanoparticles for the stabilization of o/w emulsions that will result in so-called Pickering emulsions [13]. The solid particles are able to adsorb irreversibly at the o/w interface by the action of capillary forces [14] to form a densely packed steric barrier layer [15]. This effect can, in turn, efficiently prevent drop coalescence and can result in very stable emulsions with low particle dosages [15,16]. The particles that are used for Pickering emulsions typically have amphiphilic characteristics, i.e. they have an affinity for the two phases of the emulsion [17].

Because of bio-based nanoparticles' potential inherent biodegradability, researchers have considered such nanoparticles to be especially beneficial as oil-spill response agents for promoting oil dispersion; many of the currently available soluble synthetic polymeric dispersants, in contrast, have been associated with negative health and environmental impacts [18–20]. Certain nanoparticles have been reported to possess low toxicity and reduced negative impact on marine organisms, with good stabilization performance [21]. Previously, nanoparticles that contain silica, clay, iron oxide, and carbon black, for example, have been tested in o/w emulsions, with the aim of enhancing preparedness for oil spills in deep-water seas [22]. These emulsifying particles can improve the natural biodegradability of oil by marine organisms when mechanical oil recovery is not feasible (for example, due to harsh climate conditions).

Researchers have previously used CNCs for successful Pickering emulsion stabilization in o/w interfaces in model suspensions [15–17,23–27]. CNCs' dimensions are considered to be in the optimal range for providing stable Pickering emulsions by the action of stabilizing capillary forces [28], although studies have found that their performance depends on cellulose surface characteristics [17,25]. Because CNCs typically possess mainly hydrophilic surface characteristics, they are especially viable for forming oil-in-water emulsions (water as dispersing phase), as stated by the Bancroft rule [29]. We have also reported the use of hydrophobized nanocrystals to increase the stabilization of soybean oil emulsions [10]. Because the use of functionalized CNCs as dispersants for petroleum oil spills has not yet been reported in the literature, there is significant potential in this field. The performance of CNCs in petroleum oil stabilization could potentially be further enhanced by the introduction of hydrophilic and hydrophobic functional groups, thus resulting in bifunctional structures.

In this work, the preparation and properties of marine diesel o/w emulsion stabilized by bifunctionalized cellulose nanocrystals were investigated. First, celluloses with amphiphilic characteristics were synthesized using partial, sequential periodate–chlorite oxidation and a reductive amination treatment, followed by a homogenization treatment to liberate the individual CNCs. Bifunctional CNCs with variable carboxylic and amino group contents were obtained and further characterized with transmission electron microscopy (TEM), diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy, and optical transmittance measurement. The potential of differently synthesized CNCs to act as dispersing agents in o/w emulsions was screened, and two products (*But*-CNC/A and *But*-CNC/D) were chosen for more in-depth analysis. The effects of CNC and electrolyte concentrations on emulsion stability and average oil-droplet size were studied using laser diffractometry and analytical centrifugation.

2. Materials and methods

2.1. Raw materials and chemicals

Chemical birch pulp (*Betula pendula*) was received as dry sheets that were disintegrated in deionized water according to standard procedure and used as the raw material for CNC fabrication. $NaIO_4$ (India; purity $\geqslant$99.0%) and LiCl (Germany; purity $\geqslant$98.0%) were obtained from Sigma–Aldrich for the fabrication of dialdehyde cellulose (DAC) by periodate oxidation. The chemicals used in the chlorite oxidation ($NaClO_2$ and CH_3COOH) were also purchased from Sigma–Aldrich. In the reductive amination reaction, 2-picoline borane (Sigma–Aldrich, USA [95%]) and *n*-butylamine hydrochloride (Tokyo Chemical Industry, Belgium [>98%]) were used. Ethanol (96%), obtained from VWR (Finland), was used in the washing step after the amination process. All chemicals were pro analysis grade and were used without further purification. Deionized water was used throughout the experiments in the dilutions and disintegrations; lightweight marine diesel oil was used for all o/w emulsions. The diesel oil was a sulfur-free winter-grade oil with a density of 828 kg/m^3 at 15 °C and viscosity of 1.846 mm^2/s at 40 °C (Neste Oyj, Finland).

2.2. Chemical bifunctionalization of cellulose

A sequential oxidation route, followed by reductive amination, was performed to fabricate bifunctionalized CNCs. The periodate oxidation method was initially used to modify the disintegrated birch cellulose to DAC. Oxidation was performed with two different procedures, and two diverse aldehyde contents were obtained (DAC1 and DAC2). Disintegrated cellulose (15 g oven-dry weight) was oxidized using 12.3 g of sodium periodate ($NaIO_4$) in water (1500 ml) at 65 °C for 180 min to attain DAC1 with an aldehyde content of 2.20 mmol g^{-1}. The oxidation of 15 g cellulose with 12.3 g of sodium periodate ($NaIO_4$) and 27 g of lithium chloride (LiCl) in water (1500 ml) resulted in DAC2, with an aldehyde content of 3.86 mmol g^{-1}. The determination of the aldehyde content of the DAC was based on an oxime reaction between the aldehyde group and $NH_2OH{\cdot}HCl$ [30].

Both DAC1 and DAC2 were further oxidized with a similar procedure, using sodium chlorite ($NaClO_2$) to obtain partially oxidized dicarboxylic acid cellulose (PO-DAC). Three different sodium chlorite amounts were used in the oxidation of DAC1. In this procedure, 0.497 g, 0.994 g, and 1.243 g of sodium chlorite were each diluted with 17.78 g of deionized water, then poured into three beakers with 26.65 ml of 20 vol% acetic acid. These solutions were then mixed with 2 g of DAC1 diluted in 44.4 ml of water to attain carboxylic acid contents of 0.50 mmol g^{-1}, 1.13 mmol g^{-1}, and 1.58 mmol g^{-1}, respectively. The carboxyl content was then analyzed by conductometric titration using a procedure described by Katz et al. [31] and Rattaz et al. [32].

The oxidation reaction was completed under a fume hood with continuous mixing for 8 min. The three cellulose products that were obtained were labeled PO-DAC/A, PO-DAC/B, and PO-DAC/C. The oxidation of the DAC2 was completed with two different sodium chlorite amounts—0.87 g and 2.18 g—in 17.78 g of deionized water. An amount of 26.65 ml of 20 vol% acetic acid was mixed

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