Sustainable Stabilization of Oil in Water Emulsions by Cellulose Nanocrystals Synthesized from Deep Eutectic Solvents

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Abstract

There is an urgent global need to develop novel types of environmentally safe dispersing chemicals from renewable resources in order to reduce the environmental impact of oil spills. For this goal, cellulose, the most abundant natural polymeric source, is a promising green, nontoxic alternative that could replace the current synthetic surfactants. In this study, cellulose nanocrystals (CNC) synthesized using a deep eutectic solvent (DES) and two commercially available cellulose nanocrystals were used as marine diesel oil-water Pickering emulsion stabilizers. In particular, oil in water (o/w) emulsion formation and stability of emulsified oil during storing were addressed using a laser diffraction particle size analyzer, image analysis, and oil emulsion volume examination. The particle size of the o/w reference without CNCs after dispersing was over 50µm and coalescence occurred only a few minutes after the emulsifying mixing procedure. All three investigated CNCs were effective stabilizers for the o/w system (oil droplets size under 10µm) by preventing the oil droplet coalescence over time (6 weeks) and resulting in a stable creaming layer. The CNCs prepared using green DES systems boasted performance comparable to that of commercial CNCs, and they showed effectiveness at 0.1% dispersant dosage.

Keywords coalescence; dispersing agent; nanocellulose; oil spill; o/w emulsion; stability

1. Introduction

Various surfactants and particles have been used to promote the dispersion and stabilization of oil in water (o/w) emulsions. Dispersants or emulsifying agents (which are typically soluble compounds with amphiphilic characteristics) minimize o/w interfacial energy, thus enhancing the emulsions' long-term stability (De Gennes and Taupin 1982; Abdolmaleki et al. 2016). Inorganic or petrochemical-based particles or colloids of silica, clay, calcium carbonate, hematite, polystyrene, and microgels, ranging in size from nanometers to micrometers, can all form stable particle-stabilized o/w emulsions (so-called Pickering emulsions) (Aveyard et al. 2003; Chevalier and Bolzinger 2013; Lyu et al. 2016). Pickering emulsions are abundant in nature and will become more common, for instance, in the fields of food applications (Yang et al. 2012), filled-reinforced composite materials (Wu et al. 2014), drug delivery (Fang et al. 2008), and polymer blends, because they are generally more stable against coalescence than emulsions stabilized by surfactants alone. However, mineral based nanoparticles are not commonly used in the field of oil spill response in marine environment at the moment. There are reports that for instance silica (nano)particles can be toxic to many animals (Van Hoecke et al. 2008; Elsaesser and Howard 2012; Kim et al. 2015) and due to the bioaccumulation (Yildirim et al. 2011) they can end up even in the humans, which is highly undesirable. By contrast, many biomaterials provide an

interesting source of biodegradable alternative, working as green dispersing agents in the form of nanoparticles. For example, cellulose nanocrystals (CNCs), which are rod-like, stiff nanoparticles derived from natural cellulose sources, (Carpenter et al. 2015) have recently been shown to stabilize different o/w emulsions. Also microfibrillated cellulose particles have been shown to stabilize o/w emulsions (Andresen and Stenius 2007; Xhanari et al. 2011). If these solid cellulose particles are added to an o/w emulsion mixture, they can bind to the oil-water interface and prevent the oil droplets from coalescing, thus causing the emulsion to be more stable (Kalashnikova et al. 2011; Kalashnikova et al. 2012; Kalashnikova et al. 2013; Hu et al. 2015a; Hu et al. 2015b; Hu et al. 2016; Ojala et al. 2016).

Chemical oil spill remediation techniques use emulsifying agents to disperse oil slicks to smaller droplets and promote the inherent biodegradability of oil by marine microbes (Prendergast and Gschwend 2014). For this purpose, bio-based cellulosic nanoparticles could be especially beneficial, because the cytotoxic effects of nanocelluloses has been found to be minor (Vartiainen et al. 2011; Bhattacharya et al. 2012; Alexandrescu et al. 2013; Hua et al. 2014; Malinen et al. 2014). Also, toxicity and biodegradability analyses indicate that nano-scale cellulose particles can be considered to be safe for living organisms (Lou et al. 2014; Pitkänen et al. 2014; Vikman et al. 2015; Ruka et al. 2015). By contrast, the safety of many synthetic dispersing agent formulations has been questioned, because of their potential negative health effects for humans and the marine ecosystem (Ramachandran et al. 2004; Ramachandran et al. 2006; Jung et al. 2009; Kujawinski et al. 2011; Zhang et al. 2013; Gong et al. 2014; DeLeo et al. 2015). Based on previous mentioned fact in the use of synthetic surfactants many countries like Finland, Sweden and England have banned many commercial available dispersing chemicals and this mean in practice that they are not even allowed to use in the Baltic and North Seas (<http://www.environment.fi/en-US>; Wang M. 2010). So there is need to develop novel types of environmentally safe dispersing chemicals in order to reduce the environmental impact of oil spills.

Despite functionalized nanocelluloses having shown their potential as dispersing agents in Pickering emulsions, their production requires expensive, harmful, or toxic chemicals in many cases. Consequently, new green techniques are sought to enable their sustainable production. Deep eutectic solvents (DESs) are a relatively novel class of chemicals that can function as solvents, reactants, and catalysts. DESs are often classified as ionic liquids, although they can also be obtained from non-ionic species (Wagle et al. 2014; Smith et al. 2014). Compared to ionic liquids, DESs exhibit certain advantages, such as easy preparation from two or more components without the need for separate purification steps. DESs can be obtained from readily available, bio-based, inexpensive, low-toxicity materials, which can be regenerated quite easily. Recently, the first results of DES use as a pretreatment for cellulose nanofibrillation have been reported (Sirviö et al. 2015; Sirviö et al. 2016).

The aim of this research was to investigate cellulose nanocrystals derived from a deep eutectic solvent (DES) of choline chloride and oxalic acid dihydrate as an o/w Pickering emulsion stabilizer. Two different commercially available cellulose nanocrystals (referred to as CNC-Ref1 and CNC-Ref2) were used as a reference, and their ability to serve as a marine oil dispersing agent were addressed. Natural creaming of emulsified oils was observed over time with all CNCs. Oil layer creaming is supposed to be beneficial for the purposes of oil cleaning and collecting, because a creamed oil layer is easier to skim. However, a creaming layer has been kept stable over time. Consequently, o/w creaming formation and stability of a creaming layer during storing were examined in particular.

2. Materials & Methods

2.1 Raw material and chemicals

2.1.1. Chemicals used

For all o/w emulsions, lightweight marine diesel oil was used. This diesel oil was a sulphur-free winter grade with a density of 828 kg/m³ at 15°C and viscosity of 1.846 mm²/s at 40°C (Neste Oyj, Finland). Conductivity of the marine diesel oil was very low: 0.073 µS/cm at 20°C.

All chemicals were pro analysis grade and used without further purification. In dilutions and disintegrations, deionized water was used throughout the experiments. Dissolving pulp (*softwood*) was used as a raw material for production of

DES-treated cellulose. The cellulose, lignin, and hemicelluloses content of the dissolving pulp was 96.2, 3.5, and <0.5%, respectively. Pulp was obtained as dry sheets and was used after disintegration in water. Disintegrated pulp was filtered, washed with ethanol, and dried at 60°C for 24 hours. Choline chloride and oxalic acid dihydrate were obtained from Sigma Aldrich (Germany).

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2.1.2. Cellulose nanocrystals from DES treatment

Chemical treatment of dissolved cellulose

DES was produced by mixing 63.06 g of choline chloride and 56.94 g of oxalic acid dihydrate at 100°C for approximately 30 minutes. When a clear solution was obtained, 1.2 g of dissolving pulp (*softwood*) was added, and the suspension was mixed for 6 hours. Reaction was quenched by addition of 100 ml of deionized water before the solution was filtered and finally washed with 400 ml of deionized water.

Liberation of nanocrystals from DES-treated cellulose

The DES-treated dissolved cellulose material was converted to individual nanocrystals at a solids content of 0.5 wt% and a pH of 7 (pH was adjusted using a dilute NaOH-solution) using a homogenization treatment with M-110EH-30 microfluidizer (Microfluidics, U.S.A.). Suspension was passed three times through a 400 µm auxiliary processing module (APM) and a 200 µm interaction chamber (IXC) at a pressure of 1300 bar. Afterward, the suspensions were passed three times through a combination of 400 µm APM and 87 µm IXC at a pressure of 2000 bar. The obtained CNC suspensions were clear and only slightly viscous. Samples were marked as DES-CNC.

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2.1.3. Reference cellulose nanocrystals

Two commercial CNC suspensions named *BGB natural* (*CNC-Ref1*) and *BGB ultra* (*CNC-Ref2*) were purchased from Blue Goose Biorefineries Inc., Canada. Acetate-grade dissolving pulp (*western hemlock*) was used as a raw material for BGB's CNC fabrication. BGB production process is oxidative in nature and does not involve acid hydrolysis. However, the process resulting similar size and charge to acid hydrolysis CNC but does not contain any sulfate half esters. BGB Inc. use R3TM technology (patent pending) allowing green chemistry to manufacture renewable plant biomass into individual CNCs. Washing with deionized water and concentration with ultrafiltration were the only treatments of the product after manufacturing. Both CNC reference suspensions were delivered in approximately 7% consistency and were instantly usable and dispersible to water. CNC gels from *CNC-Ref1* were slightly thicker and more opaque than *CNC-Ref2*.

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2.2. Characterization of cellulose nanocrystals

2.2.1. Transmission electron microscopy (TEM)

The morphological features of *DES-CNC* and two commercial CNCs (*CNC-Ref1* and *CNC-Ref2*) were analyzed with a Tecnai G2 Spirit transmission electron microscope (FEI Europe, Eindhoven, the Netherlands). Samples were prepared by diluting each nanocellulose suspension with Milli-Q water. A small droplet of the dilution was deposited on top of a carbon-coated copper grid, and excess sample was removed from the grid by touching the droplet with the corner of a filter paper. The samples were negatively stained by placing a droplet of uranyl acetate (2% w/v) on top of each specimen. The excess uranyl acetate was removed with filter paper as described earlier. The grids were dried at room temperature and analyzed at 100 kV under standard conditions. Images were captured with a Quemesa CCD camera, and iTEM image analysis software (Olympus Soft Imaging Solutions GMBH, Munster, Germany) was used to measure the width and length of the individual particles.

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129 2.2.2. X-ray diffraction (XRD)

130 The crystalline structure of the different CNCs was investigated using wide-angle X-ray diffraction (WAXD) and
131 determined based on the Segal method (Segal et al. 1959). Measurements were conducted on a Rigaku SmartLab 9 kW
132 rotating anode diffractometer (Japan) using Co K α radiation source (40 kV, 135 mA) ($\lambda = 0.179030$ nm). Samples were
133 prepared by pressing tablets of freeze-dried celluloses to a thickness of 1 mm. Scans were taken over a 2θ (Bragg angle)
134 range from 5° to 50° at a scanning speed of $10^\circ/\text{min}$, using a step of 0.05° . The degree of crystallinity in terms of the
135 crystallinity index (CrI) was calculated from the peak intensity of the main crystalline plane (200) diffraction (I_{200}) at
136 26.1° and from the peak intensity at 22.0° associated with the amorphous fraction of cellulose (I_{am}) (French 2014). The
137 degree of crystallinity is calculated by Equation 1.

$$138 \quad CrI = \frac{I_{200} - I_{am}}{I_{200}} \times 100\% \quad (1)$$

139 It should be noted that due to the Co K α radiation source used, the cellulose peaks have different diffraction angles
140 compared to results obtained by a Cu K α radiation source.

141

142 2.3. Preparation of o/w emulsion

143 The marine diesel o/w emulsions were prepared using the UltraTurrax mixer (IKA T25, Germany) at 7000 rpm for 15
144 min. The ratio of oil and water was 1:10 throughout the study. The 0.1% (wt) CNC-solution was diluted into the water
145 phase before oil was added and dispersed. Sodium chloride (NaCl) was used as a background electrolyte at
146 concentration of 1w/w-% (equivalent to the salinity of 171 mmol/l). Salt concentration was used to simulate the effect
147 of salinity (comparable to sea water salinity in the Baltic Sea) on dispersion stability and oil droplet size. As a reference,
148 pure o/w emulsion without the CNC addition was used.

149

150 2.4. Laser diffraction particle size analyzer

151 The changes in volumetric oil-droplet size distributions were measured with the laser diffraction particle size analyzer
152 (LS 13 320, Beckman Coulter, U.S.A.). Each sample was measured directly after dispersing and over time (in the case
153 of the stability measurement). The method enables droplet diameters from $0.04\mu\text{m}$ to $2000\mu\text{m}$ to be measured. The
154 mean droplet diameter was taken to be the volume mean diameter from 3 replicate measurements.

155 The ‘span’ was taken as a measurement of the width of the particle size distribution. It is calculated using $\text{span} =$
156 $(D(0.9) - D(0.1)) / D(0.5)$, where $D(0.9)$ is the droplet diameter for which 90% of the droplets lie below this size, $D(0.5)$ is
157 the droplet diameter for which 50% of the droplets are below this size, and $D(0.1)$ is the diameter for which only 10%
158 of the droplets are smaller than this size. The stability of emulsions was also evaluated by monitoring the emulsion
159 droplet diameter over 6 weeks with the Beckman Coulter particle size analyzer.

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161 2.5. CCD camera unit

162 The dispersed oil droplets in the flowing oil-water suspension were visualised with a high-definition CCD camera unit
163 which captured approximately 1000 individual pictures including between 100,000-200,000 individual oil droplets per
164 sample. The method itself has been described in more detail previous publications (Haapala et al. 2013; Kangas et al.
165 2014; Laitinen and Niinimäki 2014). Image analysis of individual particles was accomplished by applying a sub-pixel
166 algorithm resulting in resolution of around $1\mu\text{m}$. In this study, minimum particle size analyzed was set to be $3\mu\text{m}$ to
167 ensure that only oil droplets were included in the measurement. The photographs obtained with the CCD camera were
168 used to evaluate the particle size distribution based on the projected oil-droplet area diameter.

169 3. Results and Discussion

170 3.1. Characterization of cellulose nanocrystals

171 According to TEM images (Figure1), all the nanocelluloses that were used existed as rod-like cellulose nanocrystals.
172 The width of individual crystals typically varied from 3–8 nm, while their length ranged from 50 to 350 nm, according
173 to the image analysis. It seems that commercial crystals (*CNC-Ref1* and *CNC-Ref2*) were similar in size to DES-treated
174 crystals despite use of different wood species (*western hemlock* vs. *European softwood*) and fabrication processes
175 (oxidation vs. DES treatment). The size distributions were in line with many earlier studies (Visanko et al. 2014;
176 Laitinen et al. 2014; Laitinen et al. 2016). All nanocrystals seemed to be well-individualized from each other without
177 the formation of larger aggregates. Moreover, all suspensions remained stable during usage and storage.

178
179 **Fig. 1** Example of TEM images of a) CNC-Ref1 b) CNC-Ref2 and c) DES-CNC.

180
181 Based on WAXD analysis, all of the CNCs retained their cellulose I crystalline structure, exhibiting the main 2θ
182 diffraction angles close to 18.0° , 22.0° , and 26.1° associated with the (1–10), (110), and (200) crystalline planes. The
183 crystallinity indexes calculated according to Eq. 1 for *DES-CNC*, *CNC-Ref1*, and *CNC-Ref2*, were 68%, 70%, and 67%,
184 respectively. The original dissolving pulp (*softwood*) has CrI of 67%. X-ray diffraction patterns of different
185 nanocelluloses are presented in Figure 2.

186

187 **Fig. 2** X-ray diffraction patterns of different nanocelluloses.

188

189 The carboxyl content of CNCs was analysed by conductometric titration using a procedure described by Katz et al. and
 190 Rattaz et al (Katz et al. 1984; Rattaz et al. 2011). The carboxyl contents and conductivities of CNC samples are
 191 presented in Table 1. The *DES-CNC* had a carboxylic acid contents of 0.23 mmol g⁻¹ while the reference *CNC 1* and
 192 *CNC 2* had values of 0.09 mmol g⁻¹ and 0.15 mmol g⁻¹, respectively. Therefore, all CNCs had a relative low surface
 193 charge density, which likely decreased their hydrophilicity (compared to, for instance, acid hydrolysed CNCs) and
 194 improved their potential as effective emulsion stabilizers (Kalashnikova et al. 2011; Kalashnikova et al. 2012;
 195 Kalashnikova et al. 2013). On the other hand, the small surface charge density was enough to prevent the inherent
 196 aggregation tendency of CNCs and the samples remained stable during storage. Conductivity variations between
 197 different samples were likely affected mainly due to small amount of impurities in dilution water. DES-CNC has been
 198 diluted with deionized laboratory water while commercial CNCs (CNC-Ref1 and CNC-Ref2) contain tap water and that
 199 is why conductivities were slightly higher.

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Table 1 Characteristics of CNC samples. Carboxyl content, type of emulsion, mean droplet diameter and “span” (measured by LS 13 320 Beckman Coulter) for fresh diesel oil emulsions stabilized by 0.1 wt-% CNCs. (The span is calculated as described in Chapter 2.4.).

Dispersant	Abbreviation	Carboxyl content (mmol/g)	Conductivity ($\mu\text{S}/\text{cm}$)	Type of emulsion	Mean diameter [μm]	Span
<i>DES-CNC</i>	DES	0.23	130	o/w	9.3	2.26
<i>BGB natural</i>	CNC-Ref1	0.09	286	o/w	7.2	1.54
<i>BGB ultra</i>	CNC-Ref2	0.15	369	o/w	7.0	1.69
<i>Reference o/w</i>	REF	-	-	not stable	52.3	4.34

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3.2. O/w Pickering emulsions stabilized by different CNCs

The efficiency of dispersing agents in o/w emulsification is affected by temperature, mixing energy, and water electrolyte concentration (salinity) (Chandrasekar et al. 2006). As a conclusion of our recently published article, (Ojala et al. 2016) we selected in this study constant conditions in terms of mixing, temperature, and background electrolyte concentration (described in Chapter 2.3) in order to compare all different CNC dispersants in the same emulsification conditions. Conductivity and pH of freshly prepared o/w emulsions were 10.9 mS/cm and 7.3, respectively, for all investigated samples. Conductivity originated mainly due to salinity of background solution.

Figure 3 presents the o/w emulsions and creaming layers 4 hours after emulsification in the presence and absence of CNCs. Clearly, the reference sample without dispersant was not stable and coalescence was easily observed over time. All CNC-stabilized emulsions formed natural smooth creaming layers. However creaming are still on progress after 4 hours. The volume of original oil layer was 6.5 ml before emulsification and was again 6.5 ml 4 hours after emulsification without CNC use. The *DES-CNC* cream layer volume was 19.4 ml 4 hours after emulsification, while the reference *CNC-Ref1* and *CNC-Ref2* had values of 20.5 ml and 19.4 ml, respectively. Thus, the volumes of creaming layers were around three times larger in the presence of CNCs, compared to oil layers without any dispersant.

222

223 **Fig. 3** Example of o/w emulsions and creaming layers 4 hours after emulsification in the presence of CNC dispersant and
 224 the absence of dispersant. From left: o/w emulsion without CNC, o/w with CNC-Ref1, CNC-Ref2 and CNC-DES.
 225

226 Figure 4 presents kinetics of oil emulsion creaming when using different CNC dispersants. Formation of a cream layer
 227 was fastest during the first two hours after emulsification and was the fastest with the *CNC-Ref1*, while the *DES-CNC*
 228 and the *CNC-Ref2* showed slightly slower kinetics. In practice, volumes of cream layers reached a constant level 1 week
 229 after emulsification and after that only minor changes happened. The DES-CNC cream layer volume was 14.4 ml 10
 230 weeks after emulsification, while the reference CNC-Ref1 and CNC-Ref2 had values of 14.4 ml and 12.5 ml,
 231 respectively.

Fig. 4 Kinetics of oil emulsion creaming with different CNC dispersants. Error bars represents standard deviation of three replicates.

3.2.1. Laser diffraction particle size analyzer

A laser diffraction particle size analyzer was used to determine the average oil-droplet particle size in the marine diesel o/w emulsions stabilized by CNCs. In Table 1, type of emulsion, the mean particle diameter and “span” values of fresh emulsions stabilized by CNCs are presented.

Stabilization of emulsion with different CNCs resulted in a significant reduction in oil-droplet size compared to o/w emulsion without any dispersant. The particle size of the o/w reference without CNCs was approximately $52.3 \mu\text{m}$ and span value was 4.34, indicating very wide size distribution. This emulsion was not stable, and coalescence had already occurred some minutes after the emulsifying mixing procedure. However, all CNC-stabilized emulsions had mean droplet size less than $10 \mu\text{m}$, and they remained stable for a long period (Figure 7).

3.2.2. CCD camera unit

Oil droplets were visualised with a high-definition CCD camera unit as described in Chapter 2.6. Figure 5 shows example pictures of oil droplets after emulsification (2 min). Use of CNCs resulted in a significant reduction in oil-droplet sizes compared to o/w emulsion without any dispersant. The imaging method is very suitable for analysis of oil droplets, because droplets are round and of proper size, and contrast between background and oil droplets is clear (i.e., grey vs. black).

Fig. 5 Example pictures of oil droplets after emulsification visualized by a high-definition CCD camera unit. (REF = o/w emulsion without CNC and CNC-Ref1/CNC-Ref2/CNC-DES = o/w emulsion stabilized with CNC-Ref1, CNC-Ref2 and CNC-DES).

The photographs obtained with the CCD camera after emulsification (2 min) were analyzed and particle size distribution of oil droplets are presented in Figure 6. Over 100,000 individual oil droplets have been analyzed per sample. The particle size distribution of the o/w reference after dispersing was seen to be much broader than with CNC-stabilized emulsions. *DES-CNC* had slightly broader particle size distribution than *CNC-Ref1* or *CNC-Ref2*. All these observations are well in line with results measured by LS 13 320 Beckman Coulter (Table 1).

Fig. 6 Size distributions of oil droplet from o/w emulsions stabilized by CNCs. Minimum particle size included in image analysis was 3 μm .

3.3. Emulsions stability

An emulsion is commonly considered to be stable if it is resistant to physical changes over a practical length of time. As marine diesel oil has a lower density than water ($d = 828 \text{ kg/m}^3$ at 15°C), a creaming process was always observed. Despite the formation of a creaming layer, no droplet coalescence occurred; that is, the size and size distribution of o/w emulsion was not notably changed.

The long-term stability of o/w emulsions stabilized by CNCs (1:10) in terms of oil cream droplet coalescence was assessed by measuring the change in mean droplet size over time using a particle size analyzer (LS 13 320, Beckman Coulter). Stability results are presented in the Figure 7. The stability of the reference o/w emulsion without CNCs was poor, as already noted and discussed in the droplet-size measurement or visual observation, and significant coalescence started immediately after emulsifying procedure.

Fig. 7 Average droplet diameter o/w emulsions stabilized by CNCs cream emulsions over 6 weeks. Error bars represents standard deviation of three replicates.

Figure 7 shows that Pickering emulsions of *CNC-Ref1* and *CNC-Ref2* are extremely stable against coalescence, with minimal change in droplet size over 6 weeks, although natural creaming occurred. The *CNC-Ref1* emulsions, which had the smallest droplet sizes at the beginning, exhibit the least coalescence. Only minor droplet size increases occurred with *DES-CNC* emulsions, indicating stable emulsion (over 6 weeks' storage), which should be enough for collecting (i.e., skimming) stabilized oil in the case of an oil spill. When oil in water emulsion is skimmed away from the surface of water, it means in practice that only minor part of CNCs will be remain in the water.

Additionally, stability of all CNC Pickering emulsions were tested by shaking the samples regularly. As a result of shaking tests, all emulsions reformed stable creaming layers after a few hours, so they acted the same way as they had after the initial emulsification procedure. This phenomenon is beneficial especially for oil collecting, where a creaming layer may be exposed by wave action that tends to break up the stabilized o/w layer.

Stability of prepared emulsions was analyzed by centrifugation of samples for 5 min at 2415G for analyzing the resistance of droplets to coalescence. The o/w emulsions after centrifugation in the presence of CNCs are shown in Figure 8. All CNC-stabilized emulsions were stable after centrifugation and coalescence were not observed, i.e. no visible oil layer appeared on the surface of the emulsions.

Fig. 8 Example of o/w emulsions after centrifugation in the presence of CNC dispersant. From left: o/w with *CNC-Ref1*, *CNC-Ref2* and *CNC-DES*.

3.4. Stabilization of o/w Pickering emulsion by adsorbed CNCs

The surface coating by solid particles mainly acts against emulsified droplet coalescence. The adsorbed layer of CNCs likely forms a rigid layer around the oil droplets as previously shown (Kalashnikova et al. 2011; Jiang and Hsieh 2015; Hu et al. 2015b). Therefore, the reorganization of the surface layer required for oil droplets to merge is prevented by a mechanical barrier. Nanocellulose particles are held together at the oil-water interface by means of attractive interactions created by hydrogen bonding while capillary forces force particles to be adsorbed at the o/w liquid-liquid interface. As it can be assumed, the strong adhesion of CNCs to the interface confers high resistance to coalescence and high stability to the emulsion. This will be attributed to the particular behavior of cellulosic particles, that is, their elongated shape and the low surface charge density chemistry forming a network of isolated oil droplets covered by nanocrystals.

4. Conclusions

The CNCs fabricated in Deep eutectic solvents were successfully used as novel biochemical for aqueous Pickering emulsification of marine diesel oil. All investigated CNCs were both effective and stable emulsifier in o/w system and they reduced the oil-droplet size significantly in emulsions. The performance of *DES-CNCs* was comparable to that of commercial CNCs and they showed effectiveness at 0.1% dispersant dosage. The emulsions which have the smallest droplet sizes at the beginning exhibit the least coalescence. The complexity of the interactions between novel cellulose-based nanoparticle surfactants and different oil types is evident and thus more experiments related to the oil and dispersant dosage including emulsification energy are needed in order to complete the lack of statistical data on this issue.

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