Integrated and sustainable preparation of functional nanocellulose via formic acid/choline chloride solvents pretreatment

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Abstract Formic acid/choline chloride (F-DES), one of high-efficiency deep eutectic solvents (DES) for lignocellulose pretreatment, has great potential in the production of nanocellulose (NC). In this work, the integrated preparation of cellulose nanocrystals (CNCs) and cellulose nanofibrils (CNFs) was developed using F-DES pretreatment and the following ball milling. Then, the properties of the resultant NC products (F-NC) were comprehensively investigated. The NC samples obtained from direct ball milling and urea/choline chloride (U-DES) plus ball milling (i.e. B-NC, and U-NC, accordingly) were used for comparison. Characterization results showed that similar to U-DES, F-DES pretreatment could effectively enhance the fibrillation of cellulose and facilitate the following ball milling for the production of NC, and the yields of NC (CNCs plus CNFs) were over 95%. Yet, compared with B-NC and U-NC, F-NC with surface ester groups had better ability to stabilize the oil/water interface for further preparation of oil-in-water Pickering emulsion. In addition, F-DES has lower viscosity than U-DES. The recovery rate of F-DES reached 92% after three cycles, and the recycled F-DES without obvious increase of viscosity showed better reusability to make the whole process clean and sustainable.

Meiyan Wu and Keyu Liao have contributed equally to this work.

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Introduction

Cellulose with the structure of β-1, 4 linked D-glucose units is an abundant, sustainable and renewable resource (Yang et al. 2021). Researchers have been working on the application of cellulose and cellulose derivatives in various fields, such as membrane materials (Wu et al. 2020), packaging materials (Ferrer et al. 2017), gel materials (Ajdary et al. 2020; Liu et al. 2021b) and energy storage (Liu et al. 2021a). In recent years, nanocellulose (NC) as a nano-sized cellulosic material has attracted great attention due to its unique physicochemical properties (e.g. nanometer scale, high specific surface area, excellent mechanical properties) (Du et al. 2019; Pires et al. 2019). NC derived from the “Top down” method, mainly including rod-like cellulose nanocrystals (CNCs) and noodle-like cellulose nanofibrils (CNFs), is prepared from lignocellulose using direct chemical/mechanical treatment or chemical/enzymatic pretreatment plus post-mechanical treatment (Dufresne 2020). Generally, direct mechanical treatment method of lignocellulose requires high energy consumption (Zhang et al. 2015), and direct chemical/enzyme treatment usually needs harsh conditions (e.g. high acid concentration) or long hydrolysis time (Tang et al. 2011). Thus, chemical pretreatment plus post-mechanical treatment is a commonly used method to prepare NC.

As known, chemical pretreatment methods mainly refer to acid hydrolysis (Bian et al. 2017), oxidation treatment (Liu et al. 2016), ionic liquid treatment (Man et al. 2011), supercritical hydrolysis (Novo et al. 2015), etc. However, these methods often involve toxic, corrosive and expensive chemicals, high process cost, or chemical recovery problems (Tomé et al. 2018). In recent years, deep eutectic solvents (DES) treatment were used as a green and sustainable method for the biorefinery of lignocelluloses or the preparation of NC materials. DES with the low melting point could be simply prepared by mixing hydrogen bond donor molecule and hydrogen acceptor molecule (Abbott et al. 2001), and easily recycled by phase separation and evaporation of water (Loow et al. 2017). DES also exhibited good removal ability of hemicellulose and lignin from lignocellulose due to their excellent dissolving capacity (Liu et al. 2017). According to the previous reports, various DES, such as oxalic acid/choline chloride (Yang et al. 2019), citric acid/choline chloride (Liu et al. 2021c), urea/choline chloride (Laitinen et al. 2017b), glycerol/aminoguanidine hydrochloride (Li et al. 2018) and imidazole/triethylmethylammonium chloride (Sirvio 2018), were employed as high-efficient pretreatment solvents to prepare NC. These preparation methods and products are summarized in Tab. S1. Among them, urea/choline chloride (U-DES) pretreatment as a commonly used approach can facilitate the swelling of cellulose fibers without the dissolution and chemical structure damage of cellulose (Laitinen et al. 2017b).

Moreover, formic acid is a good hydrogen bond donor, which can mix with choline chloride to produce a new-type DES (F-DES) (Lynam et al. 2017). In previous work, the integrated production of NC (CNCs and CNFs) with tailored characteristics was achieved via formic acid hydrolysis plus the following homogenization, and formic acid was readily recycled by vacuum distillation due to its low boiling point (100.8 °C) (Lv et al. 2019). The integrated preparation of NC (CNCs + CNFs) could get a high yield of NC and reduce the production cost (Chen et al. 2016; Wang et al. 2017). However, F-DES pretreatment has only been reported for the component fractionation/pretreatment of lignocellulose to promote enzymatic saccharification (Lynam et al. 2017), and there is no report regarding the F-DES pretreatment for the integrated production of NC.

In addition, there were many mechanical treatment methods for preparing NC (Tab. S1). Especially, ball milling with relatively low process cost may be a suitable way for mechanical treatment without any congestion (Piras et al. 2019). Cellulose feedstock can be fully pulverized, mixed and homogenized under the intense friction and impact energy from the grinding balls (Karinkanta et al. 2014). Therefore, F-DES pretreatment plus ball milling post-treatment may have great potential application in the integrated preparation of NC.

Hence, in this work, we put forward an integrated method of F-DES (formic acid/choline chloride) pretreatment plus ball milling post-treatment in order
to prepare CNCs and CNFs, and this method was compared with the most studied urea/choline chloride (U-DES) pretreatment method and direct ball milling method. Furthermore, the obtained CNCs and CNFs were comprehensively characterized for comparison, and the recovery efficiency and reusable performance of DES (F-DES and U-DES) were also investigated to make the whole process clean and sustainable. In addition, the NC samples with different characteristics to stabilize the oil/water interface were also investigated for the preparation of oil-in-water Pickering emulsion. The biodegradable and nontoxic Pickering emulsion using nanocellulose may have great potential to produce food, beverage, cosmetics, medicine, etc.

Experimental

Materials

Microcrystalline cellulose (MCC, particle size ≤ 50 μm) from Aladdin Reagents (Shanghai, China) was used as raw cellulose materials. Choline chloride (99 wt%) was obtained from Henan Xingyuan Chemicals Co., Ltd. (China). Urea (99 wt%), formic acid (88 wt%) and other reagents were purchased from Sinopharm Chemical Reagent Co., Ltd. (China). All chemicals were directly used without any further purification.

Preparation method of nanocellulose samples

F-DES was prepared by mixing choline chloride and formic acid with the molar ratio of 1:2 in a round-bottom flask under 150 rpm stirring at room temperature (25 °C) for 30 min, then a clear liquid of F-DES was obtained. For comparison, U-DES was also prepared by mixing choline chloride and urea with the molar ratio of 1:2, and the liquid of U-DES was obtained after heated to 90 °C under 150 rpm stirring for 30 min in an oil bath. Then, MCC was added in F-DES and U-DES with the fiber consistency of 5 wt%, respectively. The reaction was taken place in an oil bath at 90 °C for a certain time. After that, the dispersion was centrifuged with the centrifugal force of 11,000 g for 5 min to separate the supernatant and solid residue. The solid residue was washed five times by centrifugation with 1000 g of deionized (DI) water and then the pretreated MCC samples were obtained. The pretreated MCC with F-DES and U-DES were named as F-MCC and U-MCC, respectively. The supernatant was efficiently collected by rotary evaporation at 60 °C until there was no mass change of the liquid, and then the recycled F-DES and U-DES were obtained for reuse. F-DES recycled after the first, second and third cycle were named as F-DES (R1), F-DES (R2) and F-DES (R3), respectively, and U-DES recycled after the first, second and third cycle were named as U-DES (R1), U-DES (R2) and U-DES (R3), respectively.

The recovery rates of the recycled F-DES and U-DES were calculated according to the formula (1).

\[
\text{Recovery rate}(\%) = \frac{m_2}{m_1} \times 100\% \quad (1)
\]

wherein \(m_1\) (g) is the mass of the initial DES, and \(m_2\) (g) is the mass of the recycled DES by rotary evaporation.

Afterwards, the pretreated MCC with a solid content of 25% in DI water was put into the ball milling tank containing zirconia beads, and the mass ratio of bead and MCC sample was 40:1. The sample was milled using a Planetary Ball Mill (DECO, PBM-AD-0.4L, China) with a speed of 300 rpm for a certain time. In addition, MCC was directly ball milled with the same procedure as control. The resultant NC were collected by adding 500 g of DI water, and then centrifuged with a centrifugal force of 5000 g for 5 min to separate the CNCs and CNFs (CNCs with more dispersion stability could not be precipitated under this centrifugation). All the abbreviations in this work are listed in Table 1, and the integrated preparation route of NC is shown in Fig. 1. The yields of NC samples were calculated according to the formula (2).

\[
\text{Yield}(\%) = \frac{m_4}{m_3} \times 100\% \quad (2)
\]

wherein \(m_3\) (g) is the dry mass of the initial MCC, and \(m_4\) (g) is the dry mass of the resultant NC (CNCs or CNFs).

Characterization

The Crystallinity Index \((\text{CrI})\) of the pretreated MCC powder (F-MCC and U-MCC) and the resultant NC powder was tested by an X-ray diffractometer (Bruker, D8 ADVANCE, Germany). The Ni-filtered Cu Kα radiation was generated at 80 mA and 40 kV. The
range of scattering angle \((2\theta)\) was from 10 to 40° with a scanning speed of 0.5°/min. The \(Crl\) of all samples was calculated based on the Segal Eq. (3) with the subtraction of the background (a blank run) (Segal et al. 1959).

\[
Crl = \frac{I_{200} - I_{am}}{I_{200}} \quad (3)
\]

wherein \(I_{200}\) is the maximum intensity of the diffraction from the peak (200), and \(I_{am}\) is the minimum intensity of the diffraction between 110 and 200 peaks (Du et al. 2016a).

Fourier Transform Infrared Spectroscopy (FTIR) spectra of the samples were recorded on a spectrometer (Thermo Fisher, Nicolet 6700, USA) using the KBr pellet method and the wavenumber of spectra ranged from 4000 to 500 cm\(^{-1}\). The surface morphologies of the freeze-dried samples were imaged by a Scanning Electron Microscope (SEM, Hitachi S-4800, Japan). The images of NC morphologies were obtained via a Transmission Electron Microscope (TEM, Hitachi H-7600, Japan). The TEM samples were prepared by dropping NC suspension with a consistency of 0.01 wt% on the copper network. When the droplet was air-dried at room temperature, the sample was stained with 2 wt% uranyl acetate solution for 30 min, and then the stained samples was dried at room temperature. The mean diameters of NC samples were calculated using the Nano measurer software. NC suspensions with the consistency of 0.01 wt% were treated by ultrasoundation (200 W, 40 kHz) for 30 s, and then the equivalent volume size and Zeta potential of NC suspensions were immediately tested using a Particle Size Analyzer (NanoBrook, 90Plus, USA), and the transmittance of NC suspensions was tested by a UV–Vis spectrophotometer (Hitachi, U-4100, Japan) with the wavenumber from 350 to 800 nm. The thermal stability of various samples was investigated using a thermal analyzer (Netzsch, STA449F5 Jupiter, USA) from 50 to 600 °C with a heating rate of 5 °C/min under N\(_2\) gas. The onset temperature of thermal degradation (\(T_{on}\)) was obtained using the tangent method (He et al. 2019). Moreover, the viscosity of DES and the recycled DES samples was measured by a Viscosity Tester (PerryElmer, RVA-TecMaster, Sweden), and the CNCs and CNFs samples were prepared through the same procedure using the recycled DES to investigate the pretreatment effectiveness on MCC. For investigating the performance of recycled DES, the yield of pretreated MCC using initial and recycled DES was measured based on the National Renewable Energy

| Table 1 | List of abbreviations |
| --- | --- |
| Abbreviation | Definition |
| F-DES | Formic acid/choline chloride |
| U-DES | Urea/choline chloride |
| MCC | Microcrystalline cellulose |
| U-MCC | Pretreated microcrystalline cellulose with U-DES |
| F-MCC | Pretreated microcrystalline cellulose with F-DES |
| NC | Nanocellulose |
| F-NC | Nanocellulose prepared via F-DES pretreatment plus ball-milling |
| U-NC | Nanocellulose prepared via U-DES pretreatment plus ball-milling |
| CNCs | Cellulose nanocrystals |
| CNFs | Cellulose nanofibrils |
| B-CNCs1/B-CNFs1 | CNCs or CNFs prepared via direct ball-milling for 8 h |
| B-CNCs2/B-CNFs2 | CNCs or CNFs prepared via direct ball-milling for 16 h |
| F-CNCs1/F-CNFs1 | CNCs or CNFs prepared via F-DES pretreatment plus ball-milling for 8 h |
| F-CNCs2/F-CNFs2 | CNCs or CNFs prepared via F-DES pretreatment plus ball-milling for 16 h |
| U-CNCs1/U-CNFs1 | CNCs or CNFs prepared via U-DES pretreatment plus ball-milling for 8 h |
| U-CNCs2/U-CNFs2 | CNCs or CNFs prepared via U-DES pretreatment plus ball-milling for 16 h |
| U-DES (R1/R2/R3) | Recycled U-DES after the first/second/third cycle |
| F-DES (R1/R2/R3) | Recycled F-DES after the first/second/third cycle |
Laboratory (NREL) procedure, and all tests were conducted for three times for each sample.

In addition, the CNCs and CNFs from B-NC2, U-NC2 or F-NC2 were added in the oil/water mixture containing 10 wt% oleic acid and 90 wt% DI water to discuss the ability to stabilize the oil/water interface, and the amount of CNCs or CNFs in the mixture was 0.2 wt%. Here, oleic acid was dyed by adding 0.01 wt% oil red for better observation. After ultrasonication (200 W, 40 kHz) for 90 s, the oil/water mixture was imaged by an optical microscope (Olympus, BX-4, Japan) with 20× or 40× objective. The droplet size in Pickering emulsion was calculated using the Nano measurer software. The F-NC film was prepared by vacuum filtration of F-NC suspension with a consistency of 0.1%, and then dried in an oven at 50 °C for 5 h. The water contact angle of film was tested using a contact angle goniometer (KINO, SL200B, USA) at ambient temperature.

Results and discussion

Effect of DES pretreatment on MCC

As mentioned, MCC was firstly pretreated using F-DES and U-DES for a certain time, respectively, and then ball milled to prepare NC (CNCs and CNFs). Here, F-MCC and U-MCC after ball milling for 8 or 16 h were accordingly named as F-NC1 and U-NC1, or F-NC2 and U-NC2, respectively. Similarly, MCC after direct ball milling for 8 or 16 h was marked as B-NC1 or B-NC2, respectively. CNCs and CNFs in NC samples were also named accordingly, such as F-CNCs1 and F-CNFs1 in F-NC1. All the abbreviations in this work are listed in Table 1, and the integrated preparation route of NC is shown in Fig. 1.

The digital images of the obtained DES (F-DES and U-DES) and the corresponding pretreated MCC (F-MCC and U-MCC) are shown in Fig. S1 and S2, respectively. Compared with MCC, F-MCC and U-MCC samples after DES pretreatment for 2 h showed the same crystal structure of cellulose I with the typical peaks of 14.8° (1–10), 16.5° (110), 20.4° (012), 22.6° (200), and 34.4° (004) in the XRD patterns (Fig. 2a). This phenomenon indicated that MCC treated by F-DES and U-DES had no change on crystal structure of cellulose (Ling et al. 2018). Moreover, the crystallinity index (CrI) of U-MCC remained steady basically after U-DES pretreatment for 3 h and then decreased with the further prolonged pretreatment time, while the CrI of F-MCC decreased after F-DES pretreatment for 3 h (Fig. S3). Further increasing of DES pretreatment time caused the damage of crystalline regions of cellulose, thus resulting in a clear decrease of CrI (Suopajarvi et al. 2017). According to the previous reports, the degraded cellulose could cause the increase of the viscosity of DES, which limited the further recycling and utilization of DES. For this reason, DES pretreatment time of 2 h without the clear change of CrI was employed for the subsequent experiments.
Moreover, the chemical structure of MCC before and after DES pretreatment for 2 h was also studied by FTIR spectra (Fig. 2b). In the spectra of all cellulose samples, there are two peaks at 3342 and 2899 cm\(^{-1}\) assigning to O–H bonds and C-H bonds in the cellulose chain, and the peaks appearing at 1644 cm\(^{-1}\) and 1430 cm\(^{-1}\) are attributed to O–H bonds from water and C-H bonds, respectively (Wu et al. 2020). Specially, compared with MCC and U-MCC, an absorption peak at 1720 cm\(^{-1}\) is shown in the spectrum of F-MCC, which belongs to the newly formed ester groups (Zhang et al. 2021). According to previous study, esterification reaction between cellulose and formic acid could happen in the process of formic acid pretreatment (Du et al. 2016b). As a result, the chemical structure of F-MCC is different from MCC and U-MCC, leading to the special properties of the obtained F-NC, which will be discussed in the following part.

In addition, the morphologies of MCC, U-MCC and F-MCC are shown in Fig. 2c. The surface of MCC without DES pretreatment was relative smooth and compact, while U-MCC and F-MCC after pretreatment for 2 h exhibited the disintegrated fiber with the decrease of particle size (particularly for the F-MCC sample). These results indicated that MCC was swelled and fibrillated during U-DES and F-DES pretreatment, which was helpful for the post-mechanical treatment to product NC. This result was consistent with the effect of DES on cellulose described by Tenhunen et al. (Tenhunen et al. 2017).

Effect of ball milling time on MCC

After DES pretreatment for 2 h, the obtained F-MCC and U-MCC were milled to prepare NC, and then the NC samples (B-NC, F-NC, U-NC) made from MCC, F-MCC and U-MCC were centrifuged to separate the corresponding CNCs and CNFs. In this process, ball milling time was a very important factor to influence the properties and yield of NC. With the increase of ball milling time, the fibers bundles were gradually peeled off and separated into nanofibrils under the friction actions of ball beads (Zhang et al. 2015). Thus,
MCC and U-MCC suspensions became more and more homogeneous, while F-MCC with ester groups were gradually precipitated off in 2 h (Fig. S4-S6), and the corresponding CNCs and CNFs were gradually formed. As shown in TEM images (Fig. S7), the corresponding CNCs and CNFs separated from B-NC1, F-NC1 and U-NC1 suspensions were obtained after ball milling for 8 h. However, large nanofiber aggregations could still be observed in the images of all NC samples. After ball milling for 16 h, the dimensions of nanofiber aggregations of all CNCs and CNFs samples obviously decreased (Fig. 3), and the corresponding diameter was mainly around 6–18 nm (Fig. S8). Specially, the mean diameters of CNCs and CNFs from B-NC2 were 9.3 and 14.3 nm, respectively, which were larger than that from U-NC2 (9.2 and 11.7 nm) and F-NC2 (8.3 and 10.6 nm). This result also showed that U-DES and F-DES pretreatment on MCC, especially F-DES pretreatment, could facilitate to break fiber aggregation and generate NC in ball milling process.

Moreover, the equivalent volume size of MCC samples after ball milling was used to roughly evaluate the dimensions of fiber aggregation. As can be seen in Fig. S9, the equivalent volume size of B-MCC and U-MCC exhibited a sharp decrease in the beginning of ball milling, and then a slight decrease from 2 to 16 h of ball milling was observed. Furthermore, the equivalent volume size of U-MCC was smaller than that of B-MCC because U-DES pretreatment could promote the fibrillation effect of ball milling. In addition, it was worth mentioning that the equivalent volume size of F-MCC failed to be obtained using dynamic light scattering (DLS) method due to the influence of introduced ester groups on the structure of F-MCC. Hydrophobic ester groups could lead to the flocculation of cellulose in water (Du et al. 2016b), and then produce a large number of irregular floccules over the test range of the equipment. Also, as shown in the bottom-right corner of Fig. 3, CNCs and CNFs from MCC and U-MCC exhibited better dispersibility in DI water after standing for 24 h, while CNCs and CNFs from F-MCC were completely precipitated due to its hydrophobic ester groups on the surface (Du et al. 2016a). Additionally, although the resultant CNCs and CNFs from F-MCC had poor dispersion in water, they could be well dispersed in N, N-dimethylacetamide (DMAc) and dimethyl sulfoxide (DMSO) for over three months (Fig. S10). Therefore, it is easier to obtain NC with smaller size using pretreated MCC compared to the raw MCC under the same time of ball milling. In other words, F-DES and U-DES pretreatment can efficiently reduce the time of ball milling and then save the energy consumption in the process for the preparation of NC.

Properties of the obtained nanocellulose

The properties of the obtained CNCs and CNFs samples, such as Zeta potential, Crl, thermal stability and transmittance of NC dispersion were studied in this part. As shown in Fig. 4a, Zeta potential values of all MCC samples decreased with the increasing of ball milling time at the pH value of 7. Here, all MCC samples exhibited negatively charged property in water, and Zeta potential values of all MCC samples significantly decreased in the beginning and then remained steady during milling (Seta et al. 2020). Specially, the Zeta potential value of U-MCC was lower than that of MCC and F-MCC. This was because U-DES pretreatment was helpful for deconstruction of cellulose fibers, and thus more charged groups were exposure on the surface of sample. Moreover, the Zeta potential value of F-MCC was higher than that of MCC and U-MCC due to the formation of the uncharged ester groups on its surface (Abitbol et al. 2018).

Furthermore, F-MCC with hydrophobic ester groups had poor stability in water, but it had good stability in DMAc or DMSO. The dispersion stability of NC suspension in water can also be indicated by the transmittances of NC dispersions (Fig. 4b), because the transmittances of the NC samples in aqueous solution were related to the dispersibility and particle size (Huang et al. 2020). All NC aqueous dispersions with the consistency of 0.01 wt% exhibited good light transmittance in the visible light range from 400 to 760 nm. Especially, the transmittances of NC samples after ball milling for 16 h (B-NC2, U-NC2 and F-NC2) were lower than that of NC samples after ball milling for 8 h (B-NC1, U-NC1 and F-NC1) owing to the reduced particle size and the increased hydroxyl groups on cellulose surface after long-time mechanical processing (Sirvio et al. 2016), which can also be observed in Fig. S4-S6. In addition, the transmittances of B-NC2 and U-NC2 were lower than that of F-NC2, which was because the poor dispersibility of F-NC2 in water led to the aggregations of CNCs and CNFs in
F-NC2, and thus the transmittance of the supernatant of the F-NC2 suspension increased.

Also, XRD patterns and the $CrI$ of NC samples are shown in Fig. 4c and d, respectively. It can be seen that the MCC and all NC samples conformed to the crystal form of natural cellulose I$\beta$ (Nishiyama 2009). There was a slight amorphization effect on MCC and the pretreated MCC during ball milling process (Ago et al. 2004), and the $CrI$ of B-NC1 and B-NC2 decreased by 1.8% and 4.1%, respectively, compared with MCC. Correspondingly, the $CrI$ of U-NC1 and U-NC2 decreased by 6.6% and 7.5%, respectively, compared to U-MCC, and the $CrI$ of F-NC1 and F-NC2 decreased by 2.8% and 5.4%, respectively, in comparison with F-MCC. The reduction of $CrI$ during ball milling was because part of the crystalline region of cellulose was damaged under the friction of beads in milling (Silva et al. 2012). After DES pretreatment, the U-MCC and F-MCC with smaller particle sizes were more vulnerable to be defibrillated in ball milling compared to the initial MCC with large size and more compact structure (Fig. 2c) (Karinkanta et al. 2014). Therefore, a relatively more decrease of the $CrI$ of U-MCC and F-MCC with the extension of milling time was observed in comparison with MCC.

In addition, the thermal stability of MCC and the resultant NC samples after ball milling for 16 h was further investigated using TG analysis. TG curves in Fig. 4e show that MCC and all NC samples exhibited the similar degradation trend of the weight loss, and the weight loss at 300–400 °C was related to the decomposition of cellulose and the formation of volatile substances (Du et al. 2020). For MCC, the onset temperature of thermal degradation ($T_{on}$) was 367 °C and the temperature at maximum degradation rate ($T_{max}$) was 383 °C (Fig. 4e and S11). The $T_{on}$ and $T_{max}$ of all NC samples were lower than that of MCC because of more exposed surface as well as the smaller sizes and $CrI$ values of NC samples (Wang et al. 2007). Moreover, the $T_{on}$ of CNCs samples was higher than that of the corresponding CNFs samples due to the relative high content of crystallization zone in
Fig. 4  a Zeta potential of MCC samples after ball milling. b Transmittances of NC dispersions. XRD patterns c and the crystallinity index d of NC samples. e TG curves of NC samples. f Yield of CNCs and CNFs in NC samples, the results of Ref. 1 (Suopajarvi et al. 2017) and 2 (Wang et al. 2017) were used for comparison.
CNCs (Du et al. 2020). Specially, the $T_{on}$ and $T_{max}$ of F-CNCs2 and F-CNFS2 were all lower than that of the corresponding CNCs and CNFs in B-NC2 and U-NC2. This result was because of the smaller sizes of F-CNCs2 and F-CNFS2 resulted from formic acid hydrolysis during F-DES pretreatment (Fig. 3).

Yields of CNCs and CNFs in nanocellulose samples

The yields of NC samples and the ratio of CNCs and CNFs in NC samples are one of the most important factors particularly for the large-scale integrated production. As shown in Fig. 4f, the total yields of B-NC1 and B-NC2 samples were 97.0% and 96.4%, respectively, due to the weight loss in the process of washing. The total yields of U-NC (U-NC1 and U-NC2) samples were similar to that of B-NC, while the total yields of F-NC (F-NC1 and F-NC2) samples were decreased to 95.3% and 95.2%, respectively. This phenomenon was probably because a small amount of cellulose was hydrolyzed by formic acid during F-DES pretreatment (Lv et al. 2019). Moreover, the yields of CNCs in U-NC1 and F-NC1 were 7.1% and 7.8%, respectively, which were about 3 times higher than that of B-NC1 (2.4%). Also, the yields of CNCs in U-NC2 and F-NC2 were 9.7% and 12.6%, respectively, which were 1.3 and 1.8 times higher than that of B-NC2 (7.2%). Therefore, U-DES and F-DES pretreatment were of benefit to increase the yield of CNCs in the obtained NC samples with the same ball milling time. Moreover, in all NC samples, the yield of CNCs was increased and the yield of CNFs was decreased with the extension of ball milling time. These results indicated that part of fiber-like CNFs were turned into rod-like CNCs under the ball grinding force. Compared with the previous results about the integrated preparation of NC from the bleached eucalyptus kraft pulp, the total yields (95.2%) of CNCs and CNFs prepared using F-DES pretreatment plus ball milling were obviously higher than that (72.7%) using formic acid hydrolysis (Lv et al. 2019), and slightly lower than that (98.2%) using oxalic acid hydrolysis (Chen et al. 2016). Hence, DES pretreatment plus ball milling is a controllable method to produce CNCs and CNFs with a high total yield of NC, and the ratio of CNCs and CNFs in the obtained NC samples can be adjusted by tuning the preparation conditions.

Recovery of DES

According to the previous literatures, DES can be recycled and then reused to decrease the environmental pollution and save manufacturing cost (Yang et al. 2019). Hence, U-DES and F-DES were recycled using rotary evaporation and the reusability of DES was discussed accordingly. As shown in Fig. 5a, the recovery rates of U-DES and F-DES were over 95% after the first (R1) and second cycle (R2), and about 92% after the third cycle (R3). The reducing end groups of cellulose could react with formic acid and urea (Lv et al. 2019; Tenhunen et al. 2017), leading to a slight mass loss of F-DES and U-DES. Specially, the recovery rate of F-DES was a little lower compared to U-DES due to the volatilization of formic acid in the practical reaction and recycling process.

Furthermore, the viscosity of DES was generally between 10 and 5000 cP, which was greatly affected by temperature (Abbott et al. 2004). As shown in Fig. 5b, the viscosity of U-DES sharply decreased from 500 to 50 cP with the increasing of temperature from 30 to 95 °C. However, the temperature only had a negligible influence on the viscosity of F-DES (0–50 cP). Moreover, there was no significant change in the color of the recycled U-DES and F-DES after the third cycle (R3), and the viscosity of U-DES and F-DES slightly increased with the increasing of cycle numbers due to the slight dissolution of saccharides during DES pretreatment (Morris et al. 1981). Therefore, compared with U-DES, F-DES with much lower viscosity at 30–95 °C exhibited better operational performance, which was greatly helpful to pretreat cellulose for the preparation of NC.

As reported, the high viscosity of DES could lead to the difficulties of reuse and a lower effect of pretreatment (Sirviö et al. 2019). Thus, the recycled U-DES (R3) and F-DES (R3) were reused to pretreat MCC through the same procedure, and then CNCs and CNFs samples were obtained after ball milling for 16 h. As can be seen, the mean diameter of these CNCs and CNFs prepared using the recycled DES were similar to the CNCs and CNFs prepared using fresh DES (Fig. S12). In addition, compared with MCC, the cellulose yield of all pretreated MCC using F-DES and U-DES with different cycle number only exhibited a slight decrease (Fig. S13). In other words, it could be regarded that only a very small amount of cellulose was dissolved in initial or recycled DES, and the
similar effectiveness of pretreatment on MCC was achieved using initial and recycled DES after the third cycle.

The ability of CNCs or CNFs to stabilize the oil/water interface

As known, the CNFs are more suitable to be used as adsorbing materials, and building blocks for the preparation of functional materials (e.g. cellulose nanopaper) (Wu et al. 2020), and the CNCs are more...
suitable to be used as strengthening agents (Chen et al. 2019), and the dispersing and stabilizing agents in oil/water interface due to the amphiphilicity (Laitinen et al. 2017a). Herein, the ability of the obtained CNCs and CNFs to stabilize the oil/water interface was investigated by producing oil-in-water Pickering emulsion. Based on the previous report, stable CNCs-based Pickering emulsions can be obtained in the presence of 0.1 or 0.2 wt% CNCs (prepared using sulfuric acid hydrolysis) in oil/water mixture (10/90, w/w) (Bai et al. 2018). Therefore, the CNCs or CNFs dosage of 0.2 wt% (based on the mass of oil/water mixture) was chosen to prepare Pickering emulsion in this work.

As shown in Fig. 5c, the oil (oleic acid, dyed with oil red)/water mixture (10/90, w/w) containing 0.2 wt% CNCs and CNFs samples were pink and relatively homogenous after ultrasonication. After standing for 24 h, only the mixture containing F-CNCs2 was homogenous, the mixtures containing other CNCs and CNFs samples showed the obvious delamination. From the microphotograph of the oil/water mixtures (Fig. 5d), the instable droplets with different diameter were seen in the mixture containing B-CNCs2, while only the aggregations of oil or nanofibers were observed in the mixture containing B-CNFs2, U-CNCs2 and U-CNFs2. This phenomenon was because both B-NC2 and U-NC2 with better surface hydrophilicity could hardly absorb oleic acid (Fig. 3), and then failed to obtain homogenous emulsions. Interestingly, the oil/water mixture containing F-CNCs2 could form the stabilized oil-in-water Pickering emulsion with a rather narrow distribution of droplets size around 32 μm (Fig. 5d and S14), and the mixture containing F-CNFs2 could also form oil-in-water Pickering emulsion, but this emulsion was relatively instable probably because of the relatively larger size of F-CNFs2. Therefore, compared with B-NC2 and U-NC2, F-NC2 (F-CNCs2 and F-CNFs2) had better compatibility to oil in the oil/water mixture, and exhibited better ability to stabilize the oil/water interface.

This result was probably due to the suitable hydrophilicity of F-NC with hydrophilic hydroxyl groups and hydrophobic ester groups (Du et al. 2016a). Generally, the stability of Pickering emulsion is highly dependent on the wettability, size, and concentration of emulsifier, and it is reported that the optimal water contact angle of the emulsifier particles is 70–86° or 94–110° to form oil-in-water or water-in-oil Pickering emulsion (Akartuna et al. 2008). As tested, the water contact angle of F-NC film was about 82° (Fig. S15), so that the resultant F-NC using F-DES (formic acid/choline chloride) pretreatment in this work could be more suitable for the preparation of oil-in-water Pickering emulsion compared to B-NC and U-NC products.

Conclusions

In this work, a new type F-DES pretreatment with the following ball milling were first used for the integrated preparation of CNCs and CNFs, and this method was compared with commonly used U-DES pretreatment. Results showed that U-DES and F-DES pretreatment of MCC could decrease the dimensions of fiber aggregation, which was helpful to defibrillation of the following ball milling to product NC. Compared with U-DES, F-DES with much lower viscosity exhibited better usability and pretreatment effect to obtain the F-NC with smaller diameter, and a similar recovery rate after three cycles. Moreover, the recycled F-DES (after third cycle) also exhibited comparable pretreatment effectiveness on MCC for the preparation of NC. Therefore, the F-DES pretreatment and the following ball milling is a green, efficient, and sustainable method for the production of NC with a high yield (95%) from cellulose materials under mild conditions.

In addition, compared with B-NC and U-NC samples, the F-NC had surface ester groups, leading to a poor dispersibility in water but very good dispersibility in DMAc and DMSO. Due to the unique surface characteristics, the F-NC exhibited better ability to stabilize the oil/water interface for the preparation of oil-in-water Pickering emulsion. F-NC may also have great potential to be used as a building block in plastic/rubber systems or advanced materials.

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Declarations

Conflict of interest The authors reported no declarations of interest.

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