

## Application of micro- and nanocrystalline cellulose

**Yu S Sotnikova<sup>1,2</sup>, T S Demina<sup>1,2</sup>, A V Istomin<sup>1</sup>, G P Goncharuk<sup>1</sup>, Ch Grandfils<sup>3</sup>,  
T A Akopova<sup>1</sup>, A N Zelenetskii<sup>1</sup> and P G Babayevsky<sup>2</sup>**

<sup>1</sup> Enikolopov Institute of Synthetic Polymer Materials, Russian Academy of Sciences, 70, Profsoyuznaya str., 117393, Moscow, Russia;

<sup>2</sup> Moscow Aviation Institute (National Research University), 4, Volokolamskoe shosse, 125993, Moscow, Russia

<sup>3</sup> Interfaculty Research Centre on Biomaterials (CEIB), University of Liège, Chemistry Institute, B6C, Allée du 6 août 11, B-4000 Liege (Sart-Tilman), Belgium.

Email: detans@gmail.com

**Abstract.** Micro- and nanocrystalline forms of cellulose were extracted from flax stalks and evaluated in terms of their applicability for various materials science tasks. It was revealed that both form of cellulose had anisometric morphology with length of 27.1  $\mu\text{m}$  and 159 nm; diameter of 8.7  $\mu\text{m}$  and 85 nm, respectively. They were used as reinforcing fillers for fabrication of composite films based on hydroxyethylcellulose. Film-forming and mechanical properties of the composite materials were significantly varied in dependence on filler content (0–10 wt.%) and size. As a second option of micro- and nanocrystalline cellulose application, a study of their effectiveness as stabilizing agents for oil/water Pickering emulsions was carried out. In contrast to micron-sized cellulose the nanocrystalline form appeared to be successful in the process of  $\text{CH}_2\text{Cl}_2$ /water interface stabilization and fabrication of polylactide microparticles via oil/water Pickering emulsion solvent evaporation technique.

### 1. Introduction

Cellulose is a natural occurring linear homopolysaccharide, which is widely applied for fabrication of paper, packing, coatings, composites, etc. Among other modifications of cellulose, its micro- and nano-sized forms attract growing attention due to the improved properties, which they could bring to composite materials [1]. Micro- and nanocrystalline cellulose are produced by extraction of crystalline regions from native cellulose using acid hydrolysis of disordered/amorphous regions, which link together assemblies of microfibrils [2]. As a function of cellulose origin and processing conditions, the extracted crystalline regions could significantly vary in size and aspect ratio, although they are normally anisometric. Micro-sized cellulose is mainly used as texturizing agent and for formulation of solid pharmaceuticals dosage forms, i.e. tablets [3], while nanocrystalline cellulose is intensively studied for fabrication of mesoporous and smart (shape-memory and optical-tunable) materials [4, 5]. Nevertheless, the main application area of micro- and nanocrystalline cellulose is a reinforcing filling of composite materials, especially films and membranes used in food packaging industry [6–8]. Another promising application of cellulose particles is emulsion stabilization, which could be even more effective than that in a case of application of molecular surfactants [9, 10]. These, so-called Pickering, emulsions stabilized by solid particles instead of surfactants possessed a high resistance to coalescence and could be successfully used for food industry as well as for fabrication of core-shell nano/microparticles for drug or cell delivery [11, 12].



Thus, the work aims to fabrication of micro- and nanocrystalline forms of flax stalks cellulose and evaluation of their applicability as reinforcing fillers in composite hydroxyethylcellulose films as well as stabilization agents for oil/water Pickering emulsions, including ones used for preparation of polylactide microparticles through oil/water solvent evaporation technique.

## 2. Materials and methods

### 2.1. Materials

Micro- and nanocrystalline cellulose was extracted from bleached flax stalks cellulose (APK "Vologodchina", Russia). Hydroxyethylcellulose marked as Natrosol 250HHR (Hercules Inc., USA) was used as received. Poly(L,L-lactide) (PLLA) with an average molecular weight of 160 kDa was purchased from Sigma-Aldrich.

### 2.2. Preparation and characterization of micro- and nanocrystalline cellulose

The micro- and nanocrystalline cellulose were obtained by acidic hydrolysis and marked as MCC and NCC, respectively. Briefly, MCC was extracted from flax stalks cellulose by hydrolysis in 10% HNO<sub>3</sub> using an ecoclave Buchi ("Buchi AG", Switzerland) at temperature of 120°C, pressure of 4 MPa for 120 min [13]. The obtained MCC was washed with distilled water on membrane filter until neutral pH was reached. Nanocrystalline cellulose (NCC) was extracted from the MCC by its additional hydrolysis in a mixture of 10% H<sub>2</sub>SO<sub>4</sub> and 10% H<sub>2</sub>O<sub>2</sub> using the ecoclave at temperature of 100–105°C and pressure of 5 MPa under a simultaneous mechanical stirring at 3000 rpm for 120 min. Then, the NCC was washed with distilled water on membrane filter with pores of 100 nm until pH reached to 6.5–7. As a final step, 1 wt.% suspension of the extracted NCC was treated with ultrasound at 1 kW and 44 kHz for 20 min.

Morphology and size distribution of the obtained MCC was evaluated by optical microscopy using Levenhuk D320 L ("Levenhuk", Russia) and analyzed using ImageJ (National Institute of Health, USA) software. Morphology characterization of NCC was carried out using atomic-force microscopy NtegraPrima ("NT-MDT", Russia) as published in [14].

### 2.3. Fabrication and characterization of hydroxyethylcellulose films filled with micro- and nanocrystalline cellulose

Hydroxyethylcellulose films filled with various amount (0–10 wt.%) of MCC or NCC were cast from 1 wt.% hydroxyethylcellulose water solutions. The MCC and NCC in a form of water dispersions were added to the polymer solutions by mixing using a four-blade propeller stirrer for 10 min at 700rpm. The obtained MCC/NCC dispersions in hydroxyethylcellulose solutions were cast on polystyrene Petri dishes and, then, dried in a dust-free chamber at RT (about 48 hours). The thickness of the films was  $60 \pm 20$  μm.

Mechanical properties of the film samples were evaluated using a AGS-H universal tensile machine (Shimadzu, Japan) at a speed of 1 mm/min after films conditioning in a desiccator over a (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> saturated water solution.

### 2.4. Preparation and characterization of polylactide microparticles stabilized with micro- and nanocrystalline cellulose

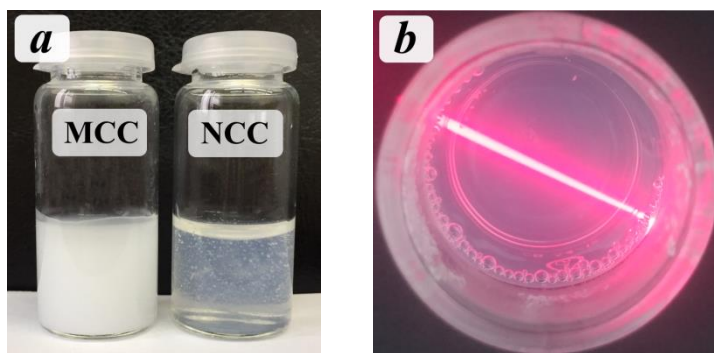
A possibility to use MCC and NCC for stabilization of oil/water emulsions was evaluated for simple CH<sub>2</sub>Cl<sub>2</sub>/water emulsions as well as for fabrication of polylactide microparticles via oil/water solvent evaporation technique. Simple oil/water emulsions were prepared as follows: 2 mL of CH<sub>2</sub>Cl<sub>2</sub> was added to 18 mL of water dispersion of NCC or MCC and mixed using a four-blade stirrer at a rotation speed of 700 rpm for 10 min. The effectiveness of oil/water interface stabilization was evaluated visually and optically. Poly(L,L-lactide) (PLLA) microparticles stabilized with NCC were prepared via Pickering oil/water emulsion solvent evaporation technique as follows: 6 wt. % solution of PLLA in CH<sub>2</sub>Cl<sub>2</sub>:acetone (9:1 v/v) was rapidly added to NCC water dispersion (0.1 – 1 wt.%) to achieve oil/water phase ratio as 1/9 v/v. The mixing of the phases was carried out using a four-blade stirrer at a rotation speed of 700 rpm until a full evaporation of the organic solvents. The obtained

solid PLLA microparticles were collected, washed several times with deionized water and fractionated using sieves with apertures of 400, 315, 200 and 100  $\mu\text{m}$ ; then, freeze-dried and weighted.

### 3. Results and discussion

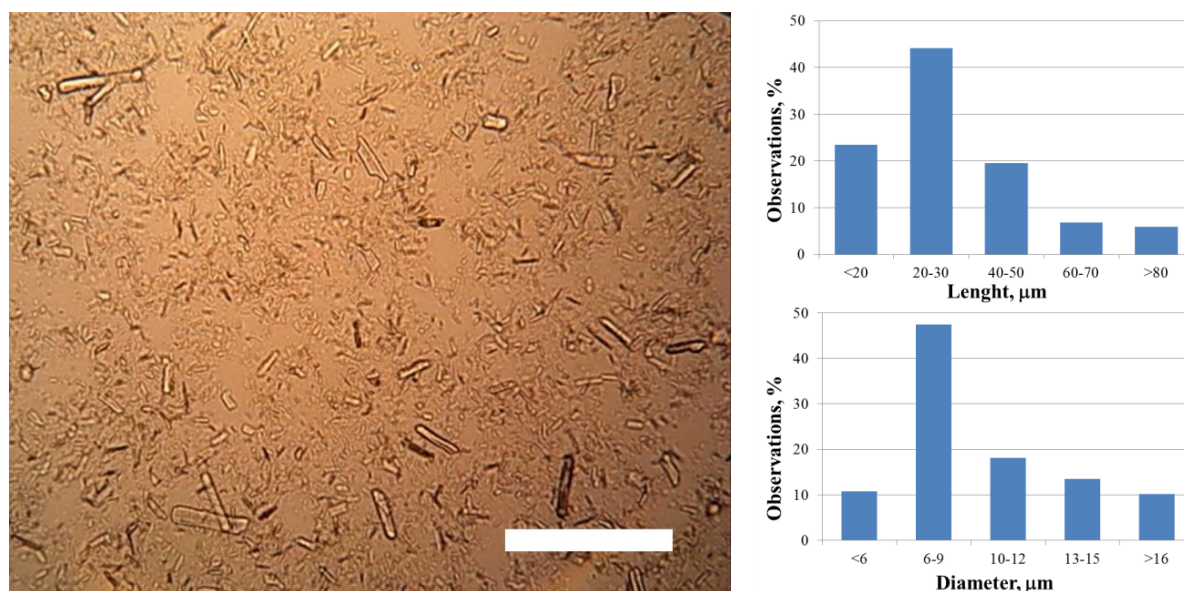
#### 3.1. Preparation and characterization of micro- and nanocrystalline cellulose

Extracted micro- and nanocrystalline cellulose form suspension and colloidal opalescent water dispersion, respectively (figure 1).



**Figure 1.** Photographs of MCC and NCC water dispersions (a) and NCC dispersion under a laser beam (b).

As could be seen in figure 2 the MCC had anisometric rod-like morphology with a mean length and diameter of 27.1  $\mu\text{m}$  and 8.7  $\mu\text{m}$ , respectively. The microcrystals significantly vary in length and diameter according to calculation of their size distribution. A study of NCC by atomic-force microscopy has also revealed anisometric morphology with a mean length and diameter of  $85 \pm 39$  nm and  $159 \pm 89$  nm, respectively [13]. Therefore, microcrystalline cellulose possessed higher aspect ratio than its nanocrystalline form: 3.1 and 1.9, respectively.

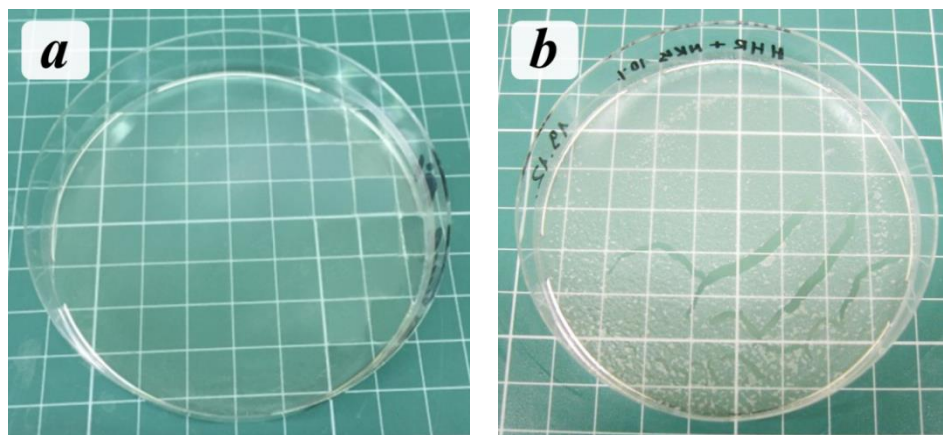


**Figure 2.** Optical micrographs of 0.5 wt.% MCC water dispersion and histograms of MCC length and diameter distributions. Scale bar is 500 $\mu\text{m}$ .

#### 3.2 Fabrication and characterization of hydroxyethylcellulose films filled with micro- and nanocrystalline cellulose

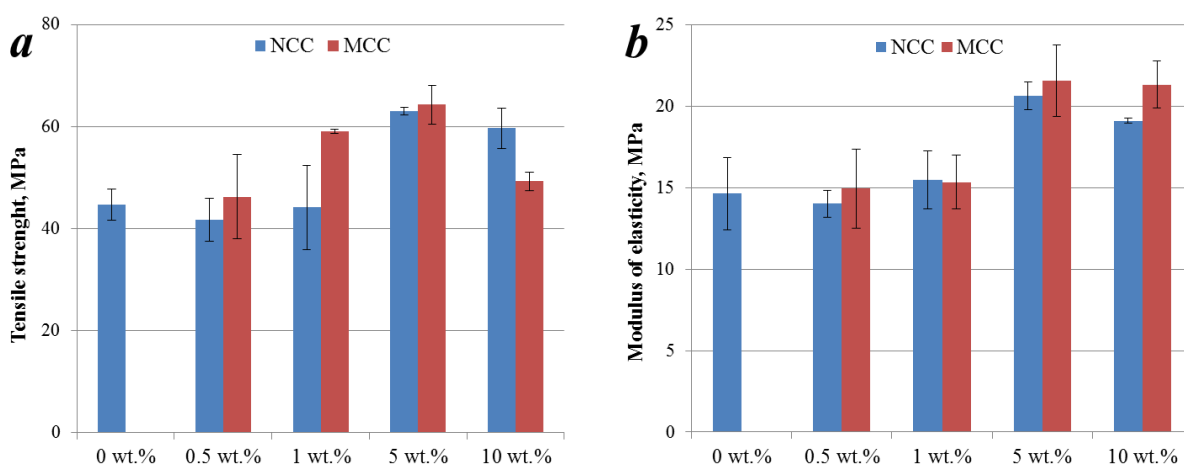
Here we investigated an effect of filling of hydroxyethylcellulose films with MCC and NCC at various concentrations on their mechanical properties. In contrast to the neat hydroxyethylcellulose film and one filled with NCC, the presence of MCC at relatively high concentrations (5–10 wt.%) led

to a cracking of films after the preparation, which could be caused by accumulation of internal stress on MCC/polymer interface during a solvent evaporation process and higher adhesion to Petri dish (figure 3).



**Figure 3.** Photographs of hydroxyethylcellulose films filled with 10 wt.% of NCC (a) and MCC (b).

The study of the filling on mechanical properties showed that both NCC and MCC had similar positive effect on films tensile strength and modulus of elasticity. As could be seen in figure 4 this effect of filling has an optimum at 5 wt.% content of NCC or MCC, when tensile strength increased up to 41–44% and modulus of elasticity up to 41–47% in comparison with neat hydroxyethylcellulose film. Previously, the extracted NCC was also used as reinforcing filler for fabrication of guar-based films and showed an filling optimum at 0.5–1 wt.% [14]. Apparently, the optimum is determined by filler distribution effectiveness over a polymer matrix, i.e. by filler concentration, polymer nature and composite films preparation conditions, while filler size (MCC or NCC) affects film-forming properties.



**Figure 4.** Tensile strength (a) and modulus of elasticity (b) of the hydroxyethylcellulose films filled with micro- and nanocrystalline cellulose at various concentrations.

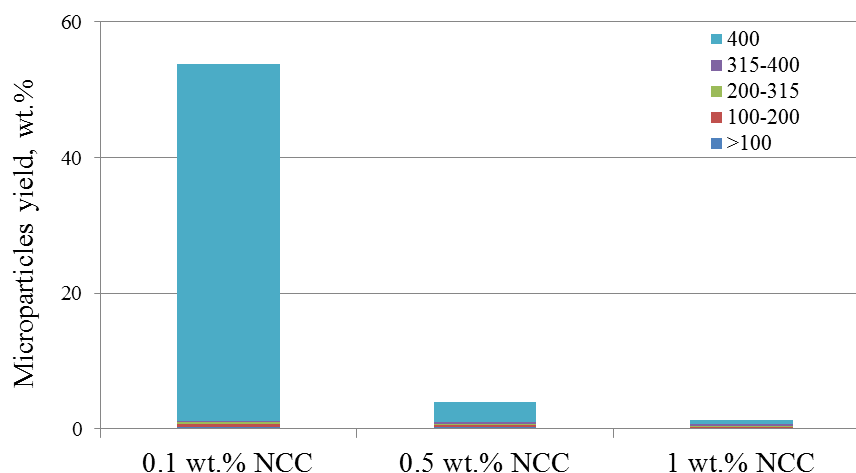
Thus, both MCC and NCC could be successfully used as reinforcing fillers for fabrication of composite films. However, the presence of micron-sized MCC leads to significant decrease in film-forming abilities of hydroxyethylcellulose, which makes NCC more suitable filler for fabrication of films and membranes, for example, in packaging industry.



### 3.3. Preparation and characterization of polylactide microparticles stabilized with micro- and nanocrystalline cellulose

A study of applicability of the MCC and NCC for stabilization of Pickering emulsions was evaluated for simple  $\text{CH}_2\text{Cl}_2$ /water system as a first step. In comparison with nanocrystalline cellulose MCC couldn't provide the interface stabilization at the described conditions, which is rather predictable due to micron-sized particles are rarely effective for Pickering emulsions. Surprisingly enough, NCC showed pronounced ability to stabilize  $\text{CH}_2\text{Cl}_2$ /water emulsions only at lower concentration (0.1 wt. %) in aqueous phase, while its increase up to 0.5–1 wt.% led to a phase separation. We assume that this decisive decrease of stabilization effectiveness could be caused by aggregation of the nanocrystals in water dispersions. As it was previously shown using dynamic light scattering the NCC at low concentration (0.1 wt. %) had mean particle size of ~60 nm, while an increase of their concentration up to 1 wt.% led to a formation of aggregates with a size up to 6.5  $\mu\text{m}$  [14]. Thus, along with aggregation the NCC lost their stabilizing ability.

An effectiveness of MCC and NCC to stabilize an interface during the fabrication of polylactide microparticles through an oil/water solvent evaporation technique was in a good agreement with results obtained using the previously discussed simple system. The polylactide microparticles were successfully fabricated only in the case of application of 0.1 wt.% NCC dispersions as aqueous phase. As could be seen in figure 5 the total yield of the produced microparticles was reached up to 54 wt.%; however, the particles had rather large mean size and their yield was drastically decreased with increase of NCC concentration in the aqueous phase. Apparently, NCC stabilization effectiveness, i.e. resistance to aggregation, could be controlled by its surface modification or adjustment of pH/ionic strength of aqueous phase.



**Figure 5.** The total yield and size distribution of polylactide microparticles prepared using NCC at various concentration in aqueous phase (**b**).

Therefore, nano-sized form of cellulose, i.e. nanocrystalline cellulose at low concentration, could effectively stabilize oil/water emulsions, including ones tailored for fabrication of polymeric particles through solvent evaporation technique. Aggregation of the nanocrystals at higher concentrations as well as application of microcrystalline cellulose led to dramatic decrease in their stabilization effectiveness.

## 4. Conclusions

Micro- and nanocrystalline flax stalks cellulose possessed anisometric particle morphology and could be used as fillers for fabrication of reinforced composite materials and stabilizing agents for oil/water Pickering emulsions. Application of both types of cellulose allowed to increase mechanical

properties of composite hydroxyethylcellulose films up to 41–47% at optimal filling content of 5 wt.%. Nanocrystalline cellulose showed higher effectiveness as agents for interface stabilization than micron-sized cellulose and allowed to fabricate polylactide microparticles through oil/water Pickering emulsion solvent evaporation technique with total yield up to 54 wt.%

## 5. References

- [1] Siro I and Plackett D 2010 *Cellulose* **17** 459-494
- [2] Habibi Y et al. 2010 *Chem. Rev* **110** 3479-3500
- [3] Thoorens G et al. 2014 *Int J Pharm* **473** 64-72
- [4] Huang J et al. 2015 *Polysaccharide-Based Nanocrystals: Chemistry and Applications* (Wiley-VCH Verlag GmbH & Co.) p 328
- [5] Lin N et al. 2012 *Nanoscale* **4** 3274-3294
- [6] Samir M A S A et al. 2005 *Biomacromolecules* **6** 612-626
- [7] Siqueira G et al. 2010 *Polymers* **2** 728-765
- [8] Miri N E et al. 2015 *Carbohydr. Polym* **129** 156-167
- [9] Chevalier Y and Bolzinger M-A 2013 *Colloids Surf A Physicochem Eng Asp* **439** 23-34
- [10] Rayner M et al. 2014 *Colloids Surf A Physicochem Eng Asp* **458** 48-62
- [11] Kalashnikova I et al. 2011 *Langmiur* **27** 7471-7479
- [12] Rescignano N et al. 2015 *J Colloid Interface Sci.* **445** 31-39
- [13] Istomin A V et al. 2016 *Fibre Chem* **48** 199-201
- [14] Sotnikova Yu S et al. 2017 *Fibre Chem* **49** 188-194