Novel Ionic Liquid-Mediated Technologies for the Extraction of Nanocellulose Directly from Wood

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Abstract

The current environmental concerns generate an increasing interest for the extraction and processing of bio-based polymers and materials. Among these is Nanocellulose. Cellulose Nanocrystals (CNCs), one form of nanocellulose, is a high-value nanomaterial with very interesting properties: light weight (density = 1.6 g/cm^3) with an elastic modulus higher than that for Kevlar fibers (110-220 GPa for CNCs, 125-130 GPa for Kevlar) (Moon, Martini et al. 2011). It also lends itself for a wide range of functional modifications and organizational patterns. Therefore, CNCs has been explored for many applications from automotive industry, membranes, to tissue engineering and pharmaceutical formulation. The production methods of CNCs have varied a lot with the sulfuric acid hydrolysis developed by Ranby in 1949 being the most famous till now. However, all these methods share one main disadvantage; they all require pure forms of cellulose, such as pulp and microcrystalline cellulose, as a starting material. In other words, no reports exist for the direct extraction of CNCs from lignocelluloses such as wood. Such approach, we believe, would foster the production and use of CNCs. In this work, ionic liquids (ILs) are proposed to ensure the multiple functions of delignifying wood and hydrolyzing wood amorphous holocellulose while at the same time preserving cellulose native crystallinity to liberate the cellulose crystallites in the form of nanocrystals.

To screen ionic liquid candidates for this objective, swelling and viscoelastic studies on Norway spruce wood treated with ionic liquids have been conducted. In particular, the temperature dependency and kinetics of swelling in 1-butyl-3-methylimidazolium acesulfamate ([BMIM]Ace) and in 1-ethyl-3-methylimidazolium acetate ([EMIM]OAc) were in focus. The kinetics of volumetric swelling in [BMIM]Ace yielded an E_a of 54 kJ.mol^{-1} compared to 23 kJ.mol^{-1} in [EMIM]OAc. The viscoelastic behavior of IL-swollen wood was studied by dynamic mechanical analysis, and the lowest *in situ* glass transition temperature (*Tg*) of lignin was ~58°C and ~65°C in [BMIM]Ace and in [EMIM]OAc, respectively. These T_g values are lower than that found in water. Higher T_g was calculated by the Gordon-Taylor equation, which means that swelling is not only due to the plasticizing effect of the ILs. SEM images showed that [EMIM]OAc has a stronger plasticizing effect than [BMIM]Ace. Overall, [EMIM]OAc is the most efficient agent for wood swelling,

softening, and disintegration and, thus, it is the most promising candidate towards the extraction of CNCs from wood.

Although the previous swelling and softening studies didn't recommend using [BMIM]Ace, a systematic kinetic and structural study of [BMIM]Ace-mediated delignification of spruce wood at 120 °C allowed shedding light on the possible interactions between wood components and this ionic liquid. Upon the treatment, wood residues and extracts were collected and thoroughly characterized with a wide range of analytical techniques. This extensive structural study evidenced prominent degradation of the acesulfamate anion into sulfate salts in lieu of the expected delignification. This unexpected behavior is explained by extensive derivatization of minute lignin extracts with the sulfate salts, which can lead to an overestimation of delignification yields.

The outcomes were more promising using [EMIM]OAc, A novel ionic liquid-based procedure to simultaneously pulp wood and liberate its cellulose as nanocrystals in 44 % yield with respect to wood cellulose content was demonstrated and proved efficient. Morphological, chemical, thermal, and surface properties evidenced the presence of partially acetylated (surface DS = 0.28) nanocrystals of native cellulose I microstructure, with a crystallinity index of about 75% and aspect ratio of 65. Direct production of CNCs from wood was ascribed to the simultaneous capability of [EMIM]OAc to (1) dissolve lignin in situ while only swelling cellulose, (2) decrease intermolecular cohesion in wood via acetylation, and (3) to catalyze cellulose hydrolysis. For improvement in nanocrystal yield, the process was optimized using Taguchi experimental design and led to an increase in yield from 44 % to about 60 % based on the wood cellulose content. This means an almost complete recovery of the original cellulose crystallites in wood.

Finally, steam explosion was used to reduce the severity of the [EMIM]OAc treatment. Steam explosion is known for its ability to hydrolyze the lignin-carbohydrate complexes in wood, which are considered to be one of the major barriers for wood utilization. Upon steam explosion, only a very mild IL treatment cycle (30 °C for 15 min) was needed to extract CNCs in a yield of 45 %, crystallinity index ca. 75 %, and remarkable aspect ratio of 83.

In summary, this dissertation reports for the first time two routes for the direct extraction of CNCs from wood: IL route, and IL route coupled with steam explosion. The high aspect ratios of the resulting CNCs together with the ease of the process and the elimination of the typically-required purification processes (such as dialysis), further position these routes as very attractive approaches in terms of process engineering and versatility for lignocellulosic biomass in general.

Thesis Outcomes:

1. H. Abushammala and M.-P. Laborie, *Ionic-liquid mediated production of cellulose nanocrystals directly from wood*, Patent application number EP15157695.6
2. H Abushammala, H. Winter, I. Krossing and M.-P. Laborie, *On the Prevalence of Side Reactions during Ionosolv Pulping of Norway Spruce with 1-butyl-3-methylimidazolium acesulfamate*, Cellulose (2014) 21: 4607-4619
3. H. Abushammala, J.F. Pontes, G.H. Gomes, A. Osorio-Madrazo, R.M.S.M. Thiré, F. V. Pereira and M.-P. Laborie, *Swelling, Viscoelastic, and Anatomical Studies of Ionic Liquid-Swollen Norway Spruce as a Screening Tool towards Ionosolv Pulping*; Holzforschung (2015) 69 (9): 1059-1067.
4. H. Abushammala, I. Krossing and M.-P. Laborie 2014, *Ionic Liquid-Mediated Technology to Produce Cellulose Nanocrystals Directly from Wood*, Carbohydrate Polymers (2015) 134: 609-616.
5. H. Abushammala, R. Goldsztayn, I. Krossing and M.-P. Laborie, *Ionic Liquid-Mediated Extraction of Cellulose Nanocrystals from Steam Exploded Wood.* Submitted.
6. H. Abushammala, I. Krossing and M.-P. Laborie, *Taguchi Optimization of One-Pot Cellulose Nanocrystals extraction from wood using ILAF*, Manuscript prepared