

Symmetric and Asymmetric End-grafted Cellulose Nanocrystals

Native plant cellulose has an intrinsic hierarchical structure. Its hydrolysis permits the isolation of nanocellulose commonly referred to as cellulose nanocrystals (CNCs), which can be utilized as building blocks for renewable nanomaterials. The promise of nanocellulose to offer new environmentally friendly solutions in the form of “nano-enhanced” and “nano-enabled” products continues to grow as a result of widespread research and development. The increased demand of CNCs has led to the development and commercialization of different CNC-types worldwide, so far, produced by ten different companies and start-ups.

Having a “known starting material” remains an important consideration, allowing for accurate comparison of material properties and research results. Therefore, within the scope of this thesis four new industrially produced CNCs were evaluated with an expanded characterization suite; two new types of sulfated CNCs and two types of carboxylic acid functionalized CNCs were compared to lab-made sulfated CNCs. Small differences in surface charge density and cellulose degree of polymerization correlated well to changes in thermal stability. Furthermore, the surface chemistry had an effect on the liquid crystalline behaviour of the CNCs.

Industrially available CNCs are all produced from cellulose I, the native crystalline allomorph of cellulose, in which the cellulose chains adopt a parallel arrangement, meaning that all of the reducing end-groups (REGs) are located at one end of a crystallite. We report the synthesis of cellulose II nanocrystals (CNC-II) via sulfuric acid hydrolysis of mercerized cellulose fibers and their physico-chemical properties and liquid crystalline behavior are compared to CNCs produced from cellulose I (CNC-I). Contrarily to cellulose I, the cellulose II allomorph adopts an anti-parallel arrangement of the cellulose chains within the crystallite, in which REG can be found on either end of a crystallite. The physico-chemical properties and the liquid crystalline arrangement of these allomorphs was studied.

Furthermore, the molecular directionality of cellulose I and II nanocrystals also permits its asymmetric and symmetric modification respectively, i.e., chemical reactions exclusively on one end or on both ends of a nanocellulose particle. To this end, the synthetic and analytical challenges related to modifying the REGs of CNCs were investigated, while proposing a path forward in addressing some of those challenges.

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