# Manufacturing of thermally stable cellulose nanocrystals by succinic anhydride assisted hydrolysis

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**1. Introduction –** Cellulose nanocrystals (CNC) have recently been demonstrated as an effective reinforcing and functional additive for polymers [1]. Hydrolysis of cellulose raw material catalysed by mineral acids is currently the most popular method for the synthesis of cellulose nanocrystals. The synthesis is typically optimized in terms of yield, dimensions and crystallinity of nanoparticles. Thus, the process involves high acid concentrations under elevated temperature that leads to the partial esterification of cellulose. Though, the presence of strong nucleofilic sulfate groups was reported as highly advantageous in terms of suspension stabilization it causes strong decrease of CNC thermal stability and limits its application to polymers that are processed well below 200°C [2].

**3. Results and Discussion** - In the current work we found that thermal and thermooxidative stability of the cellulose product diminished significantly with the increase of the acid concentration applied during hydrolysis for both sulfuric and phosphoric acids. New preparation method was proposed that allows the manufacturing of thermally stable CNC. The synthesis comprised two steps − (i) manufacturing of fine microcrystalline cellulose (MCC) by phosphoric acid catalysed hydrolysis, (ii) simultaneous hydrolysis and partial esterification of MMC with succinic anhydride (SA). The manufactured CNC-SA material showed higher thermal and thermooxidative stability than the raw cellulose material. The partial esterification of cellulose nanocrystals by the anhydride of dicarboxylic acid provided repulsive interactions of dissociated carboxyl groups that promoted the separation of individual cellulose nanocrystals. The kinetics of pyrolytic degradation of raw cellulose, CNCs produced by sulfuric and phosphoric acid catalysed hydrolysis as well as CNC modified by succinic anhydride (two step method) were studied by model-free isoconversional analysis (Friedman and Ozawa-Flynn-Wall methods). The apparent activation energy $E_a$ kept constant values during the main step of pyrolysis of the microcrystalline cellulose obtained in phosphoric acid and the nanocrystalline cellulose produced in the presence of succinic anhydride at conversion values over 0.1 showing stable mechanism of degradation. High values of $E_a$ of ca. 250 kJ/mol for CNC from sulfuric acid in the $\alpha$ range over 0.3 and CNC-SA in the $\alpha$ range below 0.1 were close to $E_a$ values reported for β-elimination pathway [3,4].

**4. Conclusions -** The presented results showed the technological potential of organic acid anhydride application for manufacturing of thermally stable cellulose nanocrystals.

**5. References**

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Current papers in the field of cellulose nanomaterials and its nanocomposites with biopolyamides for engineering application:


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2. A. Leszczyńska, K. Stafin, J. Pagacz , M. Mičušík, M. Omastova, E. Hebda , J. Pielichowski, D. Borschneck, J. Rose, K. Pielichowski, The effect of surface modification of microfibrillated cellulose (MFC) by acid chlorides on the structural and thermomechanical properties of biopolyamide 4.10 nanocomposites, *Ind. Crops Prod.* **116** (2018), p. 97-108; https://doi.org/10.1016/j.indcrop.2018.02.022
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