Toward a deeper understanding of the thermal degradation mechanism of nanocellulose

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ABSTRACT

Understanding the thermal degradation process of cellulose-nanofibers (CNF) is necessary for developing high-value added CNF-based materials with e.g. fire retardant properties or high thermal stability. This study compares the thermal degradation behavior of softwood pulp before and after TEMPO-mediated oxidation, and that of the respective CNF and TEMPO-oxidized CNF with either sodium carboxylate (T−CNF COONa) or carboxylic acid surface groups (T−CNF COOH). The cellulose materials were charred under slow pyrolysis (i.e. at 4 °C min^{-1}) from 50 °C to 600 °C using a thermogravimetric analyzer (TGA). The TGA was coupled to a mass spectrometer (MS) to analyze the volatile products evaporated during the heating process. The chemical structure and composition of the resulting chars after heating at different temperatures were assessed by infrared spectroscopy and X−ray diffraction. Fibrillation of the unmodified pulp resulted in a decrease in thermal stability of the obtained CNF, whereas TEMPO-oxidized pulp and T−CNF showed similar thermal behavior. Compared with the starting cellulose pulp, TEMPO-oxidized materials showed a reduced thermal stability. The presence of either sodium carboxylate or carboxylic acid groups influenced in particular the process of thermal degradation of the CNF. While COOH groups enhanced by 14% the thermal stability of CNF, COONa groups promoted the char formation by 27%. Tuning the counterion of T−CNF proved to be a straightforward approach for tailoring the thermal degradation behavior of the materials. The combinations of TG−MS, IR, and XRD finally resulted in the proposal of a degradation pathway for each investigated material.

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1. Introduction

Nanocellulose has intensively been investigated for the replacement of commercialized fossil-based materials by renewable, cheaper and more eco-friendly ones. Nanocellulose (cellulose nanofibers, CNF; and cellulose nanocrystals, CNC) have appealing properties such as low density, high mechanical strength, large specific surface area, and versatile surface chemistry [1]. Nanocellulose-based materials have thus been developed for a wide range of applications such as nanocomposites [2,3], paper and board coating [4–6], food-packaging [7,8], drug delivery systems [9–11], and insulating materials [12].

Compared with CNC, which are obtained by acid hydrolysis of the cellulose fibers, CNF are produced by high-shear mechanical treatment using e.g. high-pressure homogenizer, Microfluidizer®, sonication or ultra-fine grinder [13–16]. Such a strong mechanical treatment aims to fibrillate the macro-sized cellulose fibers into CNF by breaking down the strong inter-fibrillar hydrogen bonds [13]. Enzymatic or chemical pretreatments such as the TEMPO-mediated oxidation can be performed prior to the mechanical treatment for reducing the energy-consumption caused by the repeated fibrillation of the fibers [16]. Oxidation using the well-reported TEMPO/NaBr/NaClO system converts the C6 hydroxyl groups (−OH) located on the surface of the microfibrils to sodium carboxylate groups (−COONa) [1,16,17]. The introduction of negatively charged carboxylate groups leads to the individualization of the microfibrils in water by electrostatic repulsion and/or osmotic effect. After mechanical treatment, a transparent aqueous TEMPO-oxidized CNF dispersion is obtained with sodium carboxylate surface groups (T−CNF COONa), which are available for e.g. further chemical modifications.

While CNF possess outstanding properties, they usually show a lower thermal stability than the wood fibers they are made from. Compared with an initial softwood pulp, which started to degrade

at 275 °C, the thermal degradation of TEMPO-oxidized CNF occurred at 222 °C [16]. Decarboxylation of the surface carboxyl groups was proved responsible for the low thermal stability of the modified CNF [16,18]. When considering the thermal stability of non-pretreated CNF, results differ in the literature depending on the cellulose source and mechanical treatment [13–15,19]. After 120 passes using the supermasscolloider, hardwood CNF showed similar thermal degradation behavior to the untreated pulp, whereas the fibrillation treatment resulted in more thermally stable softwood CNF [19]. This result may be explained by the different amount of hemicelluloses and lignin present in the original pulps. Other studies also assigned the lower thermal stability of CNF to the larger specific surface area (SSA) exposed to heat [13–15] (and possibly to the degradation of cellulose resulting from e.g. friction of two rotating disks [19]).

In many applications such as melt compounded nanocomposites or substrates for electronic devices, an enhanced and high thermal stability is required. For the development of e.g. fire retardant materials, on the other hand, a controlled char production is demanded. Therefore, a well-studied mechanism of the thermal degradation process of nanocellulose-based materials is needed for controlling and tailoring the material properties. To date, the thermal degradation mechanism of cellulose only has been deeply investigated [20–27]. Although there exists a high number of studies reporting the thermal degradation process of cellulose, its mechanism is still not fully understood. Two competitive pathways have been proposed [21,22,26]: on one hand dehydration of cellulose occurs, resulting in the formation of anhydrocellulose, which yields by further degradation char. On the other hand, depolymerisation of cellulose yields primarily levoglucosan, which afterwards forms tar (namely, bio-oil) by further thermal degradation. These studies showed as well, that the first pathway is preferred when performing a slow pyrolysis with low heating rates (1-5 °C min^{-1}), whereas the second pathway dominates when the pyrolysis is conducted at higher heating rates (>5 °C min^{-1}).

The present study investigates the influence of the (i) fibrillation and (ii) chemical surface modification on the thermal degradation behavior of the cellulose pulp and related CNF, by slow pyrolysis under nitrogen atmosphere. The thermal degradation of the cellulose materials was assessed by thermogravimetric mass spectrometry analysis (TG–MS), infrared spectroscopy (ATR–FTIR) and X–ray diffraction (XRD). Possible pathways for the thermal degradation of the pulps and CNF are proposed and discussed, highlighting differences in thermal stability and char formation of the investigated materials.

2. Experimental section

2.1. Materials

A never-dried sulfite softwood dissolving pulp (Domsjö Dissolving Plus) based on 60% Norwegian spruce (*Picea abies*) and 40% Scotch pine (*Pinus sylvestris*), was kindly provided by Domsjö Fabriker AB (Domsjö, Sweden) and used as the original wood pulp. Before any further chemical or mechanical treatment of the pulp, the pulp was washed with hydrochloric acid (HCl) to remove impurities, and rinsed thoroughly with deionized water. Sodium bromide (NaBr), sodium hypochlorite (NaClO), 2,2,6,6-tetramethylpiperidine-1-oxyl radical (TEMPO), sodium borohydride (NaBH$_4$) and sodium carbonate (Na$_2$CO$_3$) were purchased from Sigma-Aldrich (Stockholm, Sweden) and used as received.

2.2. Methods

2.2.1. Preparation of cellulose nanofiber dispersion (CNF)

The neat pulp was suspended in deionized water at 1% w/w and homogenized at 3600 rpm at room temperature for 15 min using a High-Shear Dispermix (Ystral GmbH, Ballrechten-Dottingen, Germany). The 1 wt% suspension was then fibrillated using a MASUKO® supermasscolloider equipped with standard grindstones (MKZA10–15 J, MASUKO SANGYO CO. LTD, Saitama, Japan). From the zero contact point, a gap clearance of −100 μm was set right after pouring the suspension in the grinder. Twenty passes were performed at 30 Hz to obtain an aqueous CNF suspension at 0.84 ± 0.02 wt%.

2.2.2. Preparation of TEMPO-oxidized cellulose pulp (TOC) and TEMPO-oxidized cellulose nanofiber dispersion (T–CNF COONa)

TOC was prepared using a TEMPO/NaBr/NaClO system with 10 mmol of NaClO per gram of cellulose [1,28,29]. TEMPO-mediated oxidation was performed in water at pH 10 for 4 h. After successive washing steps using deionized water, the TEMPO-oxidized cellulose (TOC) was reduced with NaBH$_4$ (0.1 g per gram of pulp) in water at pH 10 for 3 h to convert the remaining aldehydes and ketones to hydroxyls, and prevent the heat-induced discoloration [28], followed by thorough washing with deionized water by filtration. The TOC thus obtained had a carboxylate content of 1.56 ± 0.1 mmol g^{-1}, measured by conductometric titration [29].

The T–CNF COONa dispersion (1 wt%) was obtained using the supermasscolloider as previously described. Similar parameters were used for fibrillation, but one pass only was applied (Fig. 1).

2.2.3. T–CNF with protonated carboxyl groups (T–CNF COOH)

The sodium carboxylate surface groups of T–CNF COONa were converted to protonated carboxyl groups (−COOH) by the addition of a 1 M HCl solution in a 0.1 wt% T–CNF COONa dispersion. The mixture was stirred at pH ~1, for 30 min, to obtain T–CNF COOH [30], and washed thoroughly with deionized water by filtration to obtain a T–CNF COOH suspension at 0.48 wt%.

2.2.4. Pulp and CNF foams by homogeneous freezing and ice sublimation

Foams from the unmodified pulp, TEMPO-oxidized cellulose (TOC) and respective CNF suspensions were prepared by homogeneous freezing followed by ice sublimation as follows (Fig. 1): After immersion in liquid nitrogen for 5 min, the frozen suspensions were freeze dried for 72 h at a pressure of 4-5 mbar using a freeze-dryer (Alpha 1–2 LDplus, CHRIST, Germany). The foams were then kept in a desiccator prior to thermal analyses.

2.3. Characterization

2.3.1. Thermogravimetric analysis coupled with mass spectrometry (TG–MS)

TG–MS analysis was performed on a thermogravimetric analyzer (Discovery 5500, TA Instruments, USA) coupled with a mass spectrometer (ThermoStar GSD 320, Pfeiffer, Germany). Each foam sample (dry content of ~4 mg) was heated at 4 °C min^{-1} from 50 °C to 600 °C under a nitrogen flow of 80 mL min^{-1}. From the TG and respective derivative (DTG) curves, the temperatures at 5% and 50% of weight loss ($T_{5\%}$ and $T_{50\%}$), the char content at 600 °C, and the degradation temperatures (T_{Dx}, with x corresponding to the thermal degradation stage) were determined. Using the mass spectrometer, ions of the volatile products, which were evaporated