Critical discussion on the thermal behavior of sulfated cellulose nanocrystals

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ABSTRACT: Cellulose nanocrystals (CNCs) have evolved from a laboratory curiosity to an industrial material manufactured at a scale of up to 1 ton/day. In order to maximize their use in various applications such as composites, it is critical to evaluate the influence of the surface chemistry on their thermal stability. The effect of temperature on native CNCs is heavily damaging to the material integrity, but the early stage temperature-catalyzed degradation process can be prevented by neutralization of the surface sulfate half-ester groups, either by organic or inorganic counterions. In addition, we studied the influence of the hydrolysis conditions on the CNCs' resistance to elevated temperatures. The observations were carried out by thermogravimetric analysis (TGA). Finally, complementary work regarding color formation when CNCs are exposed to heat is presented.

Application: Thermogravimetric analysis is employed to characterize the decomposition, the degradation kinetics, or the thermal stability of materials. It consists of recording the mass loss of a material as a function of temperature in a controlled atmosphere (i.e., air, vacuum, reaction gases, etc.). Our aim was to combine various approaches and propose a method for the determination of precise and accurate values of thermal stability when working with cellulosic nanocrystals.

Cellulose nanocrystals (CNCs) are rod-like particles and constitute the basic physical building blocks of cellulose, which contribute to many of the properties of wood and paper-based products. In a one-step process, CNCs are extracted from native cellulose by chemical hydrolysis under strong acidic conditions [1,2]. The surface of the crystals extracted by sulfuric acid hydrolysis bear anionic sulfate half-ester groups that provide a colloidal stability to the resulting aqueous suspensions, but are detrimental to the thermal stability of CNCs [3].

Since the pioneering work of Favier et al., CNCs have been studied as reinforcing fillers in nanocomposite applications due to their remarkable mechanical reinforcement properties [4]. Because most of the host matrices are hydrophobic, the CNC surface has to be chemically modified to make it more compatible in order to favor the interfacial properties and promote their dispersion within the bulk matrix. Surface modification of CNCs can either be done through physical (noncovalent) or chemical (covalent) bonding. The most common approaches used are adsorption, ionic bonding, oxidation, esterification, amidation, and grafting [5-7].

To benefit from these mechanical reinforcement properties, CNCs must withstand the high temperature conditions often required in the blending/processing steps with molten synthetic polymers (130°C–250°C). Additionally, since CNCs have become a commercial product, there is a need to determine the thermal stability for quality control, standardization, and optimal performance purposes. The number of cellulose-based nanomaterials produced keeps increasing (shapes: crystals, fibrils, filaments; chemical modifications: carboxylated, sulfated, etc.), and thermal stability will certainly represent a reliable way to differentiate them from each other. A major improvement was made when Wang et al. evidenced that the neutralization of sulfate half-ester groups by sodium hydroxide can significantly improve CNCs' thermal stability [8]. Typically, the sodium counterions prevent CNCs from the early-stage degradation, suggesting that other surface modifications might also have a positive impact on CNCs' resistance to high temperatures.

Thermogravimetric analysis (TGA) is a routine method for studying the thermal degradation of materials, including cellulose [3,8-17]. Thermal stability is defined as the ability of a material to maintain its physical and chemical integrity until at least one single feature (e.g., color, weight, etc.) changes upon heating. TGA is employed to characterize the decomposition, the degradation kinetics, or the thermal stability of materials. It consists of recording the mass loss of a material as a function of temperature in a controlled atmosphere (i.e., air, vacuum, reaction gases, etc.). The most widely used temperature profiles are the isothermal mode and the temperature ramping mode. Recently, Dufresne reviewed many thermogravimetric data on CNC, highlighting the complexity of comparing measurements due to the wide range of CNC materials and analytical conditions used [18]. Regardless of the nature of the sample, the TG curve is strongly dependent on the experimental conditions (mass of sample, gas atmosphere, heating rate, etc.) [19].

In this study, we combined various thermogravimetric ap-

proaches in order to propose a method for the determination of precise and accurate values with CNC materials (see Experimental Methods section). The attempt was to demonstrate the influence of the surface chemistry on the thermal stability of CNCs through the effects of:

- Hydrolysis conditions [20]
- Degree of sulfation [20]
- Use of inorganic and organic hydroxides for neutralization of sulfate half-ester groups.

In addition, we correlated the CNC coloration changes that occur upon heating to the mass loss profile obtained from TG curves. From these observations, recommendations are made considering the end-use of CNCs.

EXPERIMENTAL METHODS

CNC extraction

Aqueous CNC suspensions were prepared in the FPInnovations pilot plant (Pointe-Claire, QC, Canada) from a commercial bleached softwood kraft pulp (NBSK) according to a procedure adapted from the literature [20,21]. Milled dried pulp was added to 64 wt% sulfuric acid heated to 45°C and mixed for 25 min. The reaction was quenched with deionized (DI) water (10 x acid volume), centrifuged and dialyzed to remove residual acid, and then homogenized to ensure good dispersion. The resulting suspension was filtered and concentrated to around 5 wt%. CNC suspensions were produced at different temperatures: 45°C, 50°C, and 65°C (LT-CNC, MT-CNC, and HT-CNC, respectively). Increasing the hydrolysis temperature increases the sulfate half-ester content of the resulting CNCs as shown in **Table I**. The sulfate half-ester group content was obtained by Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES) [22]. Typically, pH of the never-dried CNC suspensions ranges between 2.5 and 3.0.

Neutralization of CNC suspensions with inorganic and organic hydroxides

The neutralization of CNC suspensions was carried out with various types of base. Inorganic hydroxides MOH with M=Na, Li, K, Cs (sodium, lithium, potassium, and cesium, respectively) were purchased from Sigma Aldrich, St. Louis, MO, USA (reagent grades), and organic quaternary ammonium hydroxides R_4NOH with R=Me, Et, Pr, Bu (methyl, ethyl, propyl, butyl, respectively) were kindly provided by Sachem Inc. (Austin, TX, USA). All chemicals were used as received. In a typical experiment, an acidic suspension of never-dried CNCs was neutralized by hydroxide solution to pH 7 unless otherwise mentioned. Neutralized CNCs are labelled as follows in the article: CNC-Na, CNC-Li, CNC-K, CNC-Cs, CNC-Me_4N, CNC-Et_4N, CNC-Pr_4N, CNC-Bu_4N.

	Hydrolysis Temperature, °C	Sulfate Half-Ester Content, mmol·kg^{-1}
LT-CNCs	45	240±10
MT-CNCs	55	260±10
HT-CNCs	65	280±10

I. Extraction conditions and sulfate half-ester groups content for cellulose nanocrystal (CNC) suspensions produced at different temperatures – low temperature (LT), medium temperature (MT), and high temperature (HT).

Sample preparation, temperature ramping and isothermal experiments conditions

After neutralization with the selected hydroxide solution, suspensions were then freeze-dried from a 2% w/w suspension. The dried material was manually pressed in a homemade mold to generate cylinder-shape pellets that perfectly fit the TGA platinum pans. The pellet dimensions were 6.6 mm in diameter and approximately 4 mm in height (compression of the freeze-dried material into pellets does not alter the measurement). Experiments were conducted using a thermogravimetric analyzer Q5000IR (TA Instruments; New Castle, DE, USA). Data was processed using Universal Analysis software (TA Instruments; New Castle, DE, USA) and the thermal stability temperatures (T_{onset} and T_{stab}).

For the isothermal conditions, the isothermal temperature was reached after rapid heating of the sample starting from room temperature up to the isothermal target temperature and then maintained at this temperature for increasing periods of time (1, 5, 15, 30, 60 min). Pictures of the heated CNC pellets were taken after each isothermal run.

RESULTS AND DISCUSSION

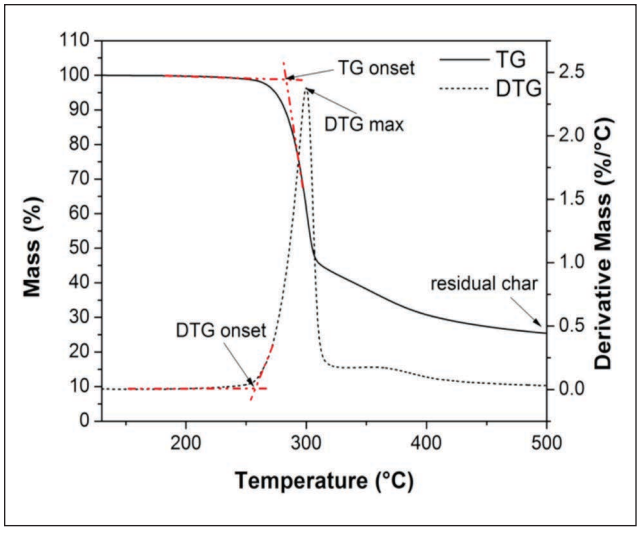
Basic knowledge about the TGA technique

The literature shows that the thermal stability (T_{stab}) can be extracted from any thermogravimetric curve (TG) or its derivative (DTG), based on these four well-accepted methods:

- Tangent method (TM), which is used to determine onset temperatures (T_{onset}) from the intercept of the tangent line of the TG or DTG curves with the tangent line corresponding to the acceleration of the degradation regime.
- ASTM E2550-07 (2012) "Standard Test Method for Thermal Stability by Thermogravimetry": T_{stab} is defined when the TG or DTG curve starts to deviate from the tangent line used to graphically determine T_{onset}.
- Maximum peak of the DTG curve derivative (DTG_{max}), which corresponds to the maximum mass loss rate reached during the degradation reaction. In the literature, DTG_{max} is often defined as T_{stab}.
- Constant mass loss method (CML): in this method, T_{stab} is defined as the temperature at which the sample has reached a predefined mass loss expressed as a percentage (generally ranging from 1% to 5%).

The T_{stab} values extracted from the thermogram shown in **Fig. 1** using these four methods are tabulated in **Table II**.

For the same sample, the four methods generate a wide



1. Typical thermogravimetric (TG) (mass, %, left axis) and derivative thermogravimetric (DTG) (derivative mass, %/°C, right axis) curves of a freeze-dried CNC-Na (CNC neutralized with NaOH) pellet in the temperature ramping mode at 10°C·min^{-1} under nitrogen gas.

range of T_{stab} values spreading from 172°C to 300°C. This discrepancy clearly illustrates the complexity to access the true value of thermal stability of a CNC sample, as evidenced by Dufresne [18]. All these methods are sensitive to the heating rate and have their own limitations:

- The ASTM method relies on the experimenter's determination of the onset temperature. The position of the tangent may also be affected by the amount of residual moisture in the sample.

Method	T_{stab}, °C	T_{stab} Value Influenced by Experimenter
ASTM – TG	186	Yes
ASTM – DTG	172	Yes
TM – TG_{onset}	277	Yes
TM – DTG_{onset}	256	Yes
DTG_{max}	300	No
CML (1%)	245	No
CML (2%)	262	No
CML (3%)	268	No
CML (4%)	271	No
CML (5%)	274	No

ASTM = ASTM E2550-07 (2012) "Standard Test Method for Thermal Stability by Thermogravimetry"; TM = tangent method; TG_{onset} and DTG_{onset} = onset temperatures of TG and DTG curves; DTG_{max} = maximum peak of DTG curve; CML = constant mass loss.

II. Comparison of the four methods used in the determination of T_{stab} (thermal stability extracted from thermogravimetric curve [TG] or its derivative [DTG]) of CNC-Na.

- The tangent method (TM) depends on the experimenter's determination of the tangent lines. Like the ASTM method, the position of the tangent lines can be affected by the amount of residual moisture in the sample. This method overestimates the temperature at which the mass loss starts decreasing.
- The maximum peak of the derivative thermogravimetric curve (DTG_{max}) method is not experimenter-dependent, as the maximum peak is calculated by the software. However, this method greatly overestimates the temperature at which CNC degradation starts because the DTG_{max} corresponds to the inflexion point of the TG curve (which at this stage represents a substantial mass loss, i.e. ~30% mass loss in Fig. 1).
- The constant mass loss (CML) method is dependent on the experimenter's own definition of the mass loss, which can vary by several percent. However, once the mass loss set point has been defined, there is no influence from the experimenter.

Among the four methods described here, the ASTM method was discarded because of the experimenter's influence on the final results. The DTG_{max} method was discarded because of a systematic overestimation of the thermal stability temperature. Finally, CML method was not retained because of its arbitrary definition of mass loss. In the subsequent sections of this article, only the results of the TM method will be shown either for temperature ramping as well as for isothermal runs.

Improved protocol

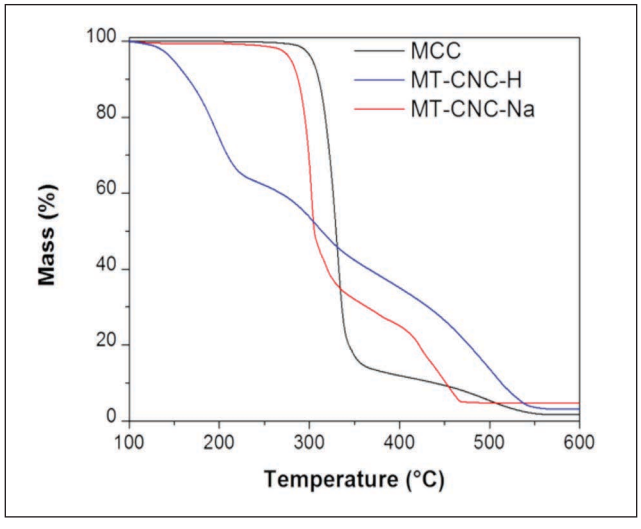
From the data listed in Table II, it is clear that determining an absolute thermal stability value from temperature ramping analysis is nearly impossible to achieve. Despite this limitation, we defined a protocol (**Table III**) that yields reproducible and consistent T_{stab} values that can be used for quality control, standardization, and nanocomposite processing conditions.

When the instrument is run in temperature ramping

Sample Preparation	Sample weight: 15 mg
	CNC physical aspect: dried CNC pressed into a small pellet
	Conditioning dried CNC in a desiccator 24 h prior to TGA run
Experimental Conditions	Temperature ramp: 10 °C.min^{-1} from 50°C to 600°C
	Gas type: air
	Gas flow rate: 25 mL.min^{-1}
	Protective gas flow rate: nitrogen at 10 mL.min^{-1}
Data Interpretation	Tangent method (TM)

III. Protocol for CNC T_{stab} determination from temperature ramping programmed thermogravimetric analysis (TGA).

mode and because of mass transfer limitations, thermal stability measured by TGA is strongly influenced by the operating parameters. According to the best practices, low heating rates (1°C·min^{-1}) give a better estimation of T_{stab} values (data not shown). A more accurate estimation of T_{stab} can, however, be obtained if the instrument is run in isothermal mode (also called annealing or aging), which consists of recording the mass loss over time upon heating at a constant temperature for a preset period of time (typically 60 min). In this study, we propose a new way to determine T_{stab} based on the combination of multiple isothermal runs performed at various temperatures. Briefly, the mass loss percentage recorded at various duration times (1, 5, 15, 30 and 60 min) is plotted as a function of the isothermal temperature. T_{stab} is then defined as the temperature at which the mass loss curve starts to deviate from linearity (the linear baseline is drawn based on the best fitting curve using the first data points measured before 200°C). More detailed information will be given throughout the text.

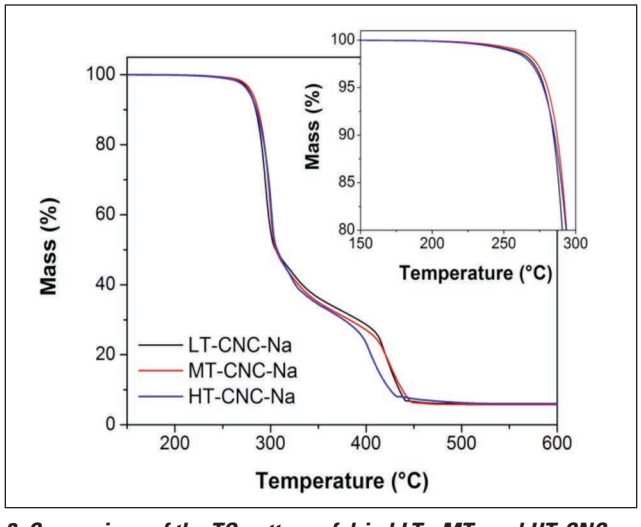


2. Influence of the presence of acidic (MT-CNC-H) and sodium salt (MT-CNC-Na) sulfate half-ester groups on dried CNC samples upon heating (microcrystalline cellulose (MCC) is used as a reference non-sulfated cellulosic material).

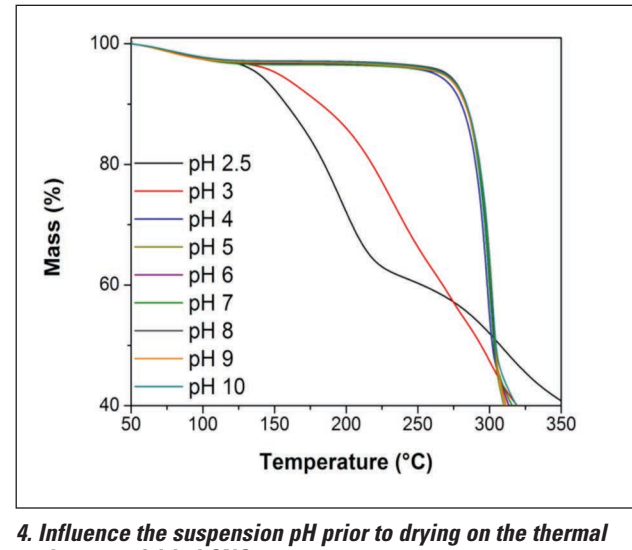
Influence of the presence of sulfate half-ester groups

Three different grades of CNCs were produced (Table I) with average degrees of sulfation ranging from 240 to 280 mmol·kg^{-1}. It was previously demonstrated that the presence of surface sulfate half-ester groups is detrimental to the stability of CNCs upon heating. More specifically, Roman and Winter noted that the loss of thermal resistance is inversely related to the sulfur content [3]. For illustration, we have compared a non-sulfated microcrystalline cellulose (MCC) to sulfated MT-CNCs samples, either acidic or neutralized with NaOH (**Fig. 2**). It is clear that the presence of acidic sulfate half-ester groups strongly alters the final thermal properties (blue vs. black line). On the contrary, when neutralized, the MT-CNC-Na curve shifts towards higher temperatures but shows a slightly different thermal degradation pattern compared to MCC (red vs. black line). This dissimilar behavior could be due to the slightly higher degree of polymerization of MCC.

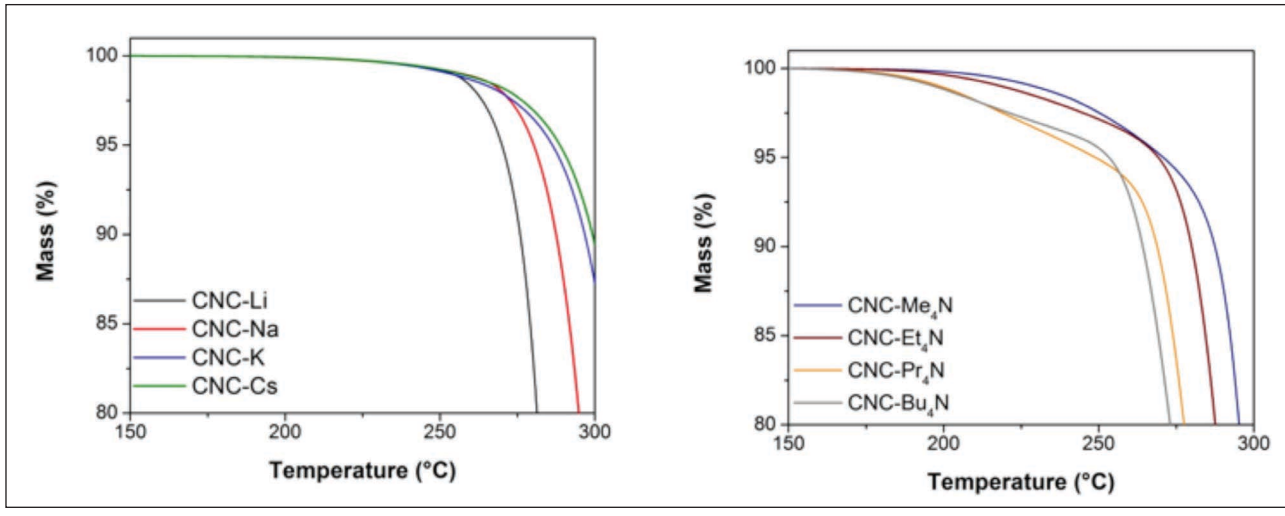
The TG curves of LT-, MT- and HT-CNC-Na are shown in **Fig. 3**. In the temperature ramping mode, there is no noticeable difference in the first degradation step (up to 300°C) in the TG curves. T_{onset} are 278°C, 279°C, and 277°C for LT-CNC-Na, MT-CNC-Na, and HT-CNC-Na, respectively. Despite the slight difference in the sulfate half-ester groups content (HT-CNCs contain 17% and 8% more half-ester, on average, than LT-CNC and MT-CNC, respectively), the results highlight that their thermal stability is identical whatever the amount of half-ester groups as long as the negative charges are neutralized (in the range 240-280 mmol.kg^{-1}). However, some differences can be observed on the second degradation step occurring after 300°C. This region is of less interest as the CNCs have



3. Comparison of the TG pattern of dried LT-, MT- and HT-CNC-Na mass loss as a function of temperature.



4. Influence the suspension pH prior to drying on the thermal resistance of dried CNCs.



5. Thermal stability/mass loss of CNCs neutralized (pH=7) with inorganic (left) and organic bases (right).

already lost 60% of their mass (from levoglucosan volatilization), and will not be discussed further. The next parts of the article will only deal with MT-CNCs.

Influence of pH adjustment using NaOH

As already mentioned, previous work has shown that the presence of the Na^+ counterion associated with the sulfate half-ester group improves thermal resistance [8]. **Figure 4** shows the mass loss profiles as a function of temperature for CNCs neutralized with increasing amounts of sodium hydroxide prior to drying.

For all samples, the mass loss observed below ~125°C is associated with the loss of adsorbed bulk water. For acidic CNCs (pH 2.5), the first degradation step is thought to be due to a desulfation process that catalyzes an acid hydrolysis of the cellulose chains [23]. The conversion of the sulfate half-ester groups into their sodium salt form prevents the desulfation process from occurring prematurely, shifting the thermal profile towards higher temperature as the pH value increases. The pH 4 curve does not superimpose over the pH 5 curve, which suggests that at pH 4, the sulfate moieties still have a negative influence on the CNC thermal degradation. At pH 5 and above, the thermal degradation pattern remains identical. It is worth noting that the presence of extra hydroxide ions at pH 7 and above is not detrimental to the thermal resistance of CNCs.

These sulfate half-ester moieties are strong acid groups; in order to guarantee that these groups exist in their salt form, the pH should theoretically be higher than pK_a+2 (i.e., 99.99% of the sulfate groups are neutralized). The stabilization of thermal behavior observed at pH 5 and above suggests that the acidity constant pK_a of CNCs is below pH 3. A series of conductometric titration experiments confirmed that the pK_a value for CNCs lies around 2.8 (data not shown). This is in agreement with the estimated pK_a (2.46) for H_2SO_4-extracted CNC found by Roman et al. [3,24]. The pK_a difference probably originates from the difference between the CNC samples (i.e., average cellulose chains molecular weight and half-ester group content).

It is also noticeable that the curve shape in the main degradation zone (below 300°C), where the mass loss rate is maximum, is different for CNCs at pH 4 compared to pH 5 and above. According to Wang et al., neutralization at pH 7 is necessary to delay the acidic sulfate half-ester catalyzed degradation, but from Fig. 4 it seems that a pH of 5 is enough to confer the maximum thermal resistance [8].

Influence of pH neutralization by other bases

Two categories of hydroxides, inorganic (alkali metal), and organic, were used to neutralize the samples (**Fig. 5**). From Fig. 5 (left), the thermal resistance (T_{onset}) of CNCs neutralized with inorganic counterions can be ranked as follows:

$K^+ \sim Cs^+ > Na^+ > Li^+$

At first, the ranking seems linked to the alkali metal ion radius: the bigger the cation, the higher the thermal stability (**Table IV**). Such an explanation for the ranking was also reported for alginates molecules in which the protons of the acidic groups were exchanged for metallic cations; the metal ions act as a flame retardant, increasing their thermal stability [25,26]. The thermal effect can also be related to the electronegativity of the alkali metal counterions (lithium provides the greatest electronegativity and cesium, the least). In this case, the more electronegative the alkali metal ion, the less thermal resistant the CNCs. This is certainly linked to the ability of less electronegative atoms to stabilize the dissociated anionic form of the sulfate half-ester group. It seems, however, that there is a limit to the increase in thermal resistance, as the effect of potassium and cesium are very similar despite their position in the periodic table (cesium, by being less electronegative than potassium, should provide a greater thermal resistance).

For organic cationic counterions (Fig. 5, right), the ranking

Type of CNC	T_{onset} Value, °C
Alkali Metal Counterions	
CNC-Li	270
CNC-Na	282
CNC-K	294
CNC-Cs	293
Organic Counterions	
CNC-Me_4N	244
CNC-Et_4N	208
CNC-Pr_4N	190
CNC-Bu_4N	184

Li = lithium; Na = sodium; K = potassium; Cs = cesium; Me_4N, Et_4N, Pr_4N, and Bu_4N = organic quaternary ammonium hydroxides R_4NOH with R=Me, Et, Pr, Bu (methyl, ethyl, propyl, butyl, respectively).

IV. T_{onset} ***of neutral forms of MT-CNCs.***

follows an opposite trend with a thermal resistance (T_{onset}) inversely proportional to the size of the counterion. The numerical values of T_{onset} are reported in Table IV.

$$Me_4N^+ > Et_4N^+ > Pr_4N^+ > Bu_4N^+$$

The explanation can find its origin in the donor inductive effect of the substituents linked to the nitrogen atom. Indeed, the alkyl substituents can then propose a greater charge density to the neighbor atom (nitrogen) it is linked to. This results in an enhanced stability of the liaison between R_4N and the sulfate half-ester group. The donor effect of such substituents is classified as follows: Me > Et > Pr > Bu, which is in agreement with the classification found for the organic counterion, where Me will greater stabilize the ionic bond between the counterion and the sulfate half-ester group.

In addition, the main degradation step occurs at lower temperature compared to that of alkali metal counterions, which is certainly due to the organic nature of the counterions. There are no published observations in the literature on similar substrates.

Another difference between the two types of counterions is the existence of two mass loss regimes for the organic ones, the first one starting at around 160°C up to 250°C. This behavior is more obvious for CNC-Pr_4 and CNC-Bu_4. The reason hidden behind this phenomenon is not yet clearly understood and may be related to the degradation of the organic cation or to the departure of the organic cation that leads to an acidification of the half-ester sulfate with a similar behavior to CNC-H.

Coloration issues and general concerns

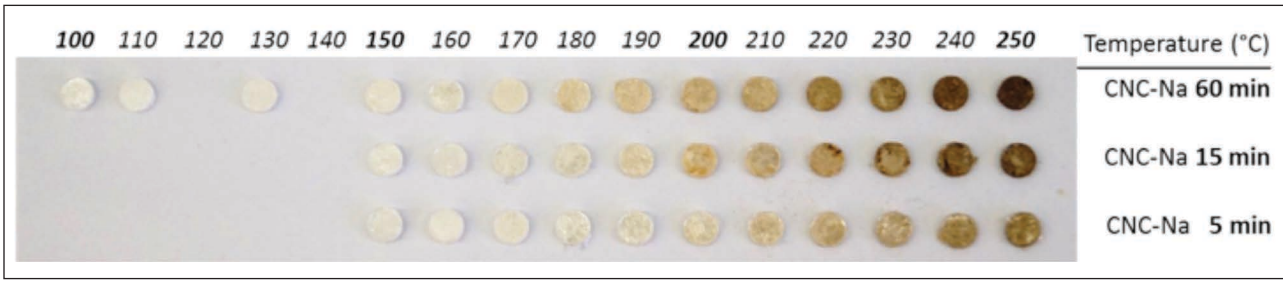
Coloration of CNC-Na as a function of temperature

Although TGA experiments give a good indication of the thermal resistance regarding the amount of material that is lost after exposure to heat, another important parameter is the coloration that occurs upon heating. The material inherently darkens more and more as it gets close to the charification temperature (above 230°C). This discoloration is of great concern for the preparation of natural-fiber reinforced polymers due to a potentially undesirable visual appearance of the final product.

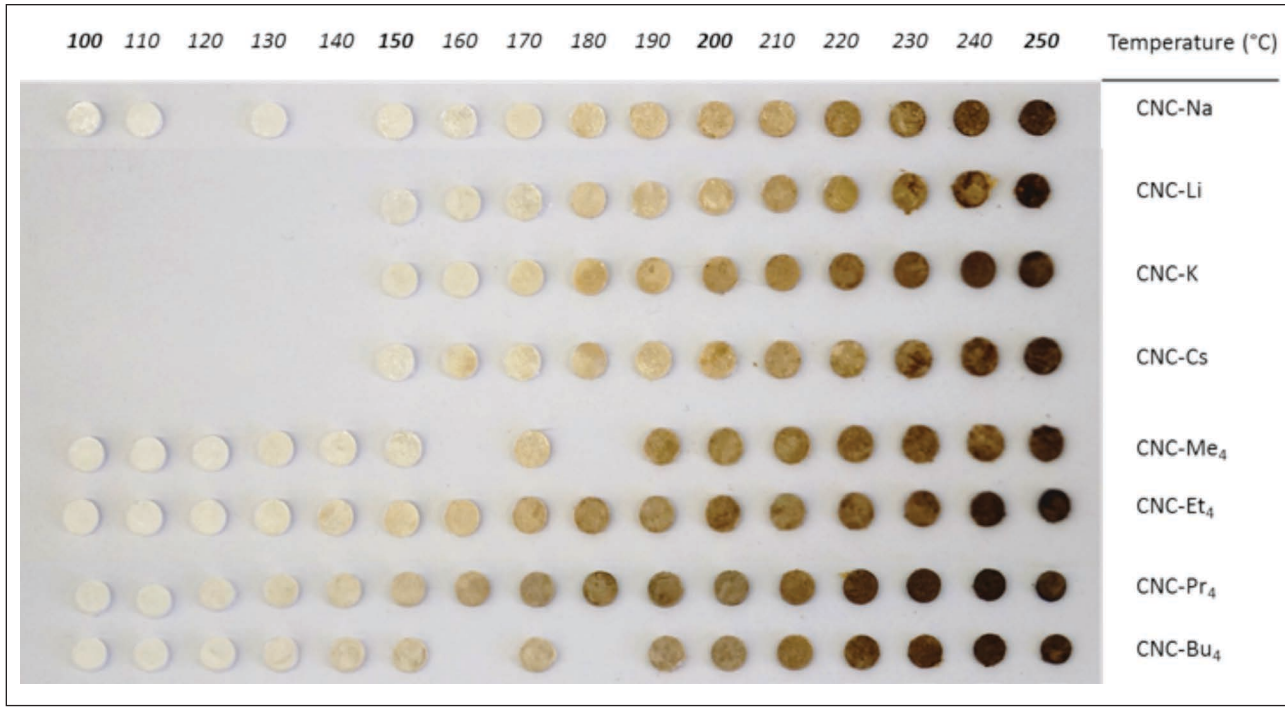
Pellets of freeze-dried CNCs were submitted to isothermal treatment for 5 up to 60 min at various temperatures ranging from 150°C–250°C (**Fig. 6**). Note that the color is observed in both inner and outer parts of the pellet.

After 60 min treatment, the discoloration of CNC-Na pellets is noticeable at temperatures around 170°C–180°C (faint beige-like tint) and the sample turns completely black at 250°C. Camarero Espinosa et al. extracted CNCs using HCl and H_2SO_4 as well as H_3PO_4 in order to compare their thermal behavior [9]. They evidenced that the presence of sulfate half-ester groups is highly detrimental to the color stability of CNCs because they catalyze the degradation at lower temperature, contrary to the HCl- and H_3PO_4-extracted CNCs. The H_2SO_4-CNCs turned black upon heating at very low temperatures (below 100°C). Such a color change does not happen for the CNCs that do not bear acidic moieties grafted at their surface (such as the HCl- and H_3PO_4-extracted CNCs). For these CNCs, the color change occurs in the same temperature range as our H_2SO_4-CNCs when neutralized in its sodium form (160°C–170°C). This confirms that the neutralization of sulfate half-ester groups is a key factor for delaying the early coloration of H_2SO_4-CNCs.

For microcrystalline cellulose substrates, it was observed that the presence of reducing ends is responsible for early



6. CNC-Na pellets discoloration as a function of the isothermal temperature (°C) and time (min).



7. Influence of counterion nature on CNC color change as a function of the isothermal temperature (60 min, in air).

stage discoloration upon heating [27]. An attempt to chemically modify the reducing end units of CNCs using either reduction or oxidation chemical reaction did not show any improvement of the thermal resistance (data not shown).

Discoloration of CNC-Na as a function of time exposure

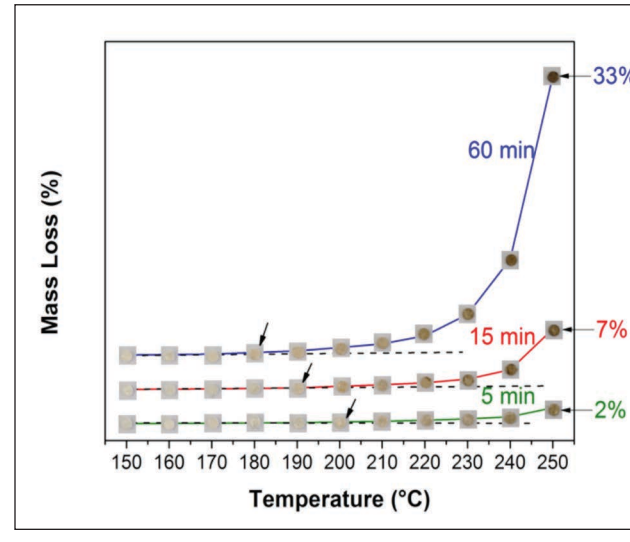
CNC-Na may be processed for time exposures shorter than an hour in industrial composite production processes. Figure 6 shows that for shorter time exposure, the color change is shifted towards higher temperatures: after 5 min at 180°C, pellets exhibit a visual aspect identical to that observed after 15 min at 170°C or 60 min at 160°C. Change in color is difficult to detect with the naked eye and a quantitative method or color evaluation device to measure whiteness (CIE with ISO standard) might be helpful.

Influence of the nature of the counterions on the color and color determination by TGA

A variation in the pellet color is observed as a function of the nature of the counterion (**Fig. 7**). The color is observed in both inner and outer parts of the pellet.

We observe that all inorganic counterions induce a color change starting at around 160°C–170°C. On the other hand, organic counterions feature a color change that occurs at lower temperature (130°C–140°C). Larger organic cations seem to be the worst, as suggested in Table IV.

Experiments for isothermal runs of CNC-Na were carried at various temperatures from 150°C–250°C and for various times (5, 15, and 60 min) and compiled in **Fig. 8**. A master curve for each time exposure was then created.



8. Master TG curve isothermal runs on CNC-Na pellets: effect of exposure time on T_{stab} (represented by an arrow).

T_{stab} can be determined from the master TG curve when the curve starts to deviate from the baseline (see arrows in Fig. 8; baseline in dashed points). After 60 min time exposure, the deviation occurs in the range 170°C–180°C, which corresponds to the same range found for the color change. Similarly, the master TG curves for the 5 min and 15 min periods indicate that the deviation occurs at greater temperatures, 180°C–190°C and 190°C–200°C, respectively. These experimental values of T_{stab} correspond to the appearance of the coloration of the samples given by isothermal runs.

SUMMARY AND CONCLUSIONS

The desired features of CNCs are linked to their chemical and physical integrity. This integrity can be affected by exposure to heat, as well as by the surface chemistry, which is particularly true when the CNCs are extracted with sulfuric acid. In their acidic form, CNCs show degradation at temperatures that are lower than the processing temperatures of most thermally extruded thermoplastics. Conversion of CNCs into their salt form (for both organic and inorganic counterions) greatly increases their thermal resistance. Beyond the mass loss associated with thermal degradation, discoloration was also observed at around 160°C for inorganic counterions and 130°C for organic counterions.

We demonstrated that the protective effect of salt conversion can be obtained at pH 5 instead of pH 7. We also demonstrated the influence of the nature of the counterion on extending the thermal stability of CNCs in dynamic heating modes. However, the T_{onset} highlighted a difference in the behavior of these counterions, with a greater protection provided by alkali metal ions compared to the organic ions.

From all these observations, we were able to draw a more accurate profile of CNC behavior upon heating. However, our study has only explored the thermal properties of the unblended dry material, which may be different when CNC-Na is blended with a polymeric matrix. The thermal behavior of dry CNCs can only be indicative of the feasibility of processing this filler under specific conditions. CNC-Na could probably be processed at temperatures higher than 170°C depending on the experimental processing conditions. For this reason, we strongly recommend that the user fine-tunes the processing conditions based on the data gathered in this paper. **TJ**

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Many reports on the thermal properties of materials can be found in the literature; however comparing the different measurements from one to the next is highly complex due to the wide range of materials and analytical conditions used. Since CNCs have become a commercial product, there is a critical need to determine the thermal stability for quality control, standardization, and optimal performance purposes. The number of cellulose-based nanomaterials produced keeps increasing (shapes: crystals, fibrils, filaments; chemical modifications: carboxylated, sulfated, etc.), and thermal stability will certainly represent a reliable way to differentiate them from each other.

CNCs have been studied as reinforcing fillers in nanocomposite applications due to their remarkable mechanical reinforcement properties. To benefit from these mechanical reinforcement properties, CNCs must withstand the high temperature conditions often required in the blending/processing steps with molten synthetic polymers (130°C–250°C). Our goal was to demonstrate that the early-stage degradation of CNCs upon heating can be prevented by using simple surface modifications. But more importantly, the main aim was to propose a method for the determination of precise and accurate values with CNC materials.

We found that determining an absolute thermal stability value from temperature ramping analysis was nearly impossible to achieve. Despite this limitation, we defined a protocol that yields reproducible and consistent thermal stability values that can be used for quality control, standardization, and nanocomposite processing conditions.

Information contained in this paper can be used to build solid data around thermal properties to be included in a quality control program or used as standardized procedures for comparison purposes.

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