Thermal Degradation of Cellulose Nanocrystals Deposited on Different Surfaces

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Summary: Thermal degradation of cellulose nanocrystals deposited on flat solid surfaces was monitored by AFM coupled with analysis of obtained images using image processor. The nanocrystals deposited on TiO_2 substrate showed different degradation patterns compared to those deposited on the nanosized layer of amorphous cellulose. The degradation was complete within 20 minutes at 300 °C. The nanocrystal deposited on amorphous cellulose resisted the heat treatment up to 120 minutes. Visual comparison and analysis of the AFM images clearly demonstrated the impact of temperature on the degradation rate of the nanocrystals deposited on TiO_2 substrate.

Keywords: atomic force microscopy (AFM); cellulose nanocrystals; image analysis; oxidation; thermal degradation

Introduction

Research of cellulose nanocrystals (CNC) has been lately receiving lots of attention in the light of recent advances and increasing interest in the field of nanomaterials. The CNC, highly crystalline rodlike particles, also termed whiskers, can be readily prepared by controlled acid hydrolysis of native cellulose. The shape, size and dimensions of the nanocrystals are primarily determined by the source of cellulose.[1,2] The dimensional characteristics of the CNCs can also be affected by hydrolysis conditions, including reaction time, temperature and acid concentration.[3] In addition, the acid used for hydrolysis was shown to have an effect on charge of the CNCs and resulting suspension properties. Two most common acids used for CNCs preparation are sulfuric and hydrochloric acids. While the CNC suspension obtained by sulfuric acid hydrolysis is very stable due to the charge on CNCs surface provided by sulfate groups introduced by esterification of the surface hydroxyl groups, the CNCs obtained by hydrochloric acid have minimal surface charges.[4,5] The sulfate groups present on the surface allows formation of stable and well dispersed aqueous suspensions of CNCs. Moreover, the sulfate-stabilized CNC suspensions exhibit a spontaneous tendency to form chiral nematic liquid crystal phases[6] – a discovery by Revol et al. in 1992 which triggered a growing number of fundamental papers about the properties of CNCs.[1,7,8]

Although the properties of CNC suspensions, particularly those obtained by sulfuric acid, have been studied extensively and they are well described in published literature[2,5,9], the thermal degradation of the CNCs has received relatively little attention. The research on thermal degradation of cellulose however, whether in its pure form or as a constituent of biomass, is enjoying renewed interest. The potential application of CNC as reinforcing filler in polymer composites[10] emphasizes the importance of understanding the behavior of CNC at elevated temperatures, considering the high temperatures commonly occurring during processing of the polymers, particularly thermoplastics.

Several literature accounts describe investigation of thermal degradation

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behaviors of CNCs, including the impact of residual sulfate groups on their thermal stability.[11] The investigations utilized thermogravimetric analysis and differential scanning calorimetry.[11,12]

The objective of this study is to elucidate the progress of CNC thermal degradation. More specifically, to visualize the crystallite size changes in the course of heat treatment. The thermal degradation of CNCs deposited on flat solid surfaces was monitored using AFM and analysis of the obtained images with image processor. Selected analytical tools allowed for studying the impact of temperature on rate of degradation by analyzing various parameters of the obtained AFM images, including crystal count, surface coverage and length of the CNCs.

Experimental Part

Materials

The base substrates were prepared from untreated silicon wafers (Si 100, Okmetic, Espoo, Finland) by cutting ca. 1×1 cm pieces and then cleaning in a UV/ozonator (Bioforce Nanosciences, Ames, Iowa) for 15 min prior to spin coating. Titania substrates were prepared by first spin coating (2800 rpm) an aqueous 0.1 M solution of titanium-(IV) bis(ammonium lactato)-dihydroxide (50 wt. % solution in water, Aldrich) onto cleaned silicon wafers. The coated films were then oxidized in an oven (600 °C; 2 hours) to TiO_2. The prepared TiO_2 surfaces were then cut to ca. 1×1 cm pieces and cleaned in a UV/ozonator for 15 min directly before spin coating cellulose nanocrystals. Cellulose substrates were prepared by spin coating (4000 rpm) trimethylsilyl cellulose solution (10 g dm^{-3} in toluene) onto untreated silica wafers and hydrolyzing the film to cellulose with 2.0 M hydrochloric acid in vapor phase. Cellulose from spruce for column chromatography (Fluka) was used as a starting material for trimethylsilyl cellulose (TMSC) synthesis. The preparation of TMSC is described in detail elsewhere.[13] The cellulose films were washed with water and dried in the spin coater just before spin coating of the cellulose nanocrystals.

Preparation, Spin Coating and Heat Treatment of Cellulose Nanocrystals

Cellulose nanocrystals were prepared from ground Whatman 541 ashless filter paper. The hydrolysis was carried out with 64 wt. % aqueous sulfuric acid at 45 °C for 45 minutes following preparation described in detail by Edgar and Gray.[14] CNC suspensions were diluted to desired concentration (100 mg dm^{-3} in water) and spin coated at 4000 rpm and acceleration of 2200 rpm/s for ca. 30 seconds. The pH value of the diluted suspension was 5.1. The heat treatment was carried out by placing the surfaces with deposited CNCs into electric muffle furnace (Select-Horn, J. P. Selecta) for selected treatment time.

Atomic Force Microscopy (AFM)

AFM was performed with a NanoScope IIIa multimode microscope (Digital Instruments Inc., Santa Barbara) in tapping mode using an E-scanner. Noncontact silicon cantilever NSG10 (NT-MDT, Moscow) with a typical force constant of 11.5 N m^{-1}, resonant frequency of 255 kHz and 10 nm radius of curvature of the tip was used for TiO_2 coated surfaces. The cellulose coated substrates were scanned with silicon cantilevers NSC15/AIBS (Ultrasharp μmasch, Tallinn, Estonia). The radius of curvature for the tip according the manufacturer was less than 10 nm, and typical resonance frequency of the cantilever was 325 kHz. For each treatment conditions at least two surfaces were treated in parallel, and at least two points on each were imaged. No image processing except flattening was performed.

Image Analysis

Average length and histograms of CNC length distribution were extracted with Scanning probe image processor (SPIP) (Image Metrology, Lyngby, Denmark) by using Threshold algorithm in the Grain Analysis feature.

Results and Discussion

The thermal degradation of cellulose nanocrystals has been studied previously using pertinent analytical techniques, including thermogravimetry, differential scanning calorimetry.[11,12] In this investigation, in addition to utilizing AFM and image analysis, the novelty of this experimental set up is that the dry individual CNC are uniformly deposited on solid surface. This work utilized previous investigation of Kontturi and coworkers on deposition of CNCs on solid surfaces by spin coating.[15] Spin coated TiO_2 and nanosized amorphous cellulose film were base substrates for CNC deposition selected for comparison of the CNC thermal degradation behavior. The TiO_2 coated silica was shown to be ideal for formation of a uniform two-dimensional dispersion of CNCs. The deposition was facilitated by the electrostatic attraction between anionic nanocrystals and cationic titania. Although the quantity of deposited CNCs on the nanosized film of amorphous cellulose was lower compared to the titania surface, the even distribution of the CNCs was comparable. This substrate was designed to mimic, to certain extent, the cellulose in its native state, where the cellulose crystalline regions are often accompanied by less ordered amorphous regions.

The TGA analysis demonstrated that the decomposition of CNCs takes place between 250 and 325 °C as a results of concurrent cellulose degradation processes such as depolymerization, dehydration, and decomposition of glycosyl units.[11] The authors also demonstrated the impact of the sulfate groups on thermal degradation of CNCs. The TGA evaluation of CNCs conducted without presence of air also showed similar thermal degradation pattern for rodlike CNCs with sulfate groups.[12] The degradation commenced at approximately 250 °C with main degradation taking place close to 300 °C. In this investigation, the objective was to visually monitor the thermal decomposition by observing the changes of the crystallite size during their exposure to heat. Based on previous studies on the thermal degradation behavior of CNCs, the temperature of heat treatment of the CNCs deposited on solid substrates was selected at 300 °C. The treatment was carried out for different length of time to observe the actual changes in CNC size during the course of the treatment. The comparison of AFM images of the CNCs deposited on titania and amorphous cellulose thermally treated at 300 °C for different lengths of time is shown in Figure 1.

Both surfaces were prepared from the same CNCs suspension of 100 mg dm^{-3} in

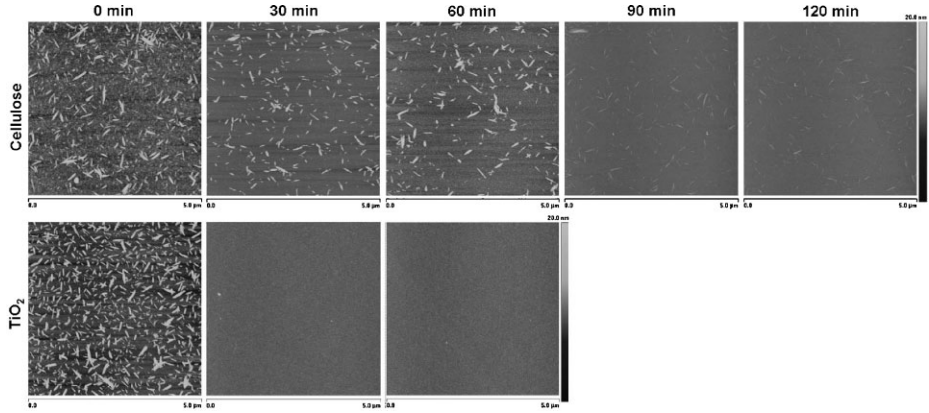

Figure 1.
$5 \times 5\ \mu m^2$ AFM height images of CNCs deposited on nanosized film of amorphous cellulose (top) and titania surface (bottom). Surfaces treated at 300°C for different length of time between 30 and 120 minutes.

water. As expected, the amount of deposited CNCs is much greater on the titania surface. After treatment of 30 minutes no CNCs were visible on the surface. In contrast, the CNCs deposited on amorphous cellulose behaved quite differently. Although a marked reduction in size and amount was observed already after 30 minutes, the subsequent reduction was significantly slower, and even after 120 minutes of the heat treatment some CNCs were still visible on the surface. Although the CNCs were expected to be degraded by the heat treatment at this temperature level, the thermal decomposition of cellulose crystallites in wood, carried out in an inert atmosphere and studied by X-ray diffraction showed that cellulose crystallites did not decompose even during 60 minutes isothermal treatment at 300 °C.[16]

As mentioned, the images of the degradation clearly demonstrated that the CNCs deposited on amorphous cellulose film can resist the heat treatment at 300 °C for an extended period of time (Figure 1). Although the titania surface is optimal for uniform deposition of CNCs, possible catalytic impact of the TiO_2 on the CNCs degradation needs to be considered. TiO_2 is a well-known oxidation catalyst and the disappearance of the crystalline cellulose in elevated temperature under atmospheric conditions is essentially an oxidation reaction. The main conclusion of this comparison is that the CNCs embedded in the nanosized film of amorphous cellulose can withstand the heat treatment of 300 °C for close to 120 minutes. In contrast, individual CNCs deposited on titania were degraded in less then 60 minutes.

To better evaluate the degradation of CNCs deposited on titania, an additional evaluation was designed to focus on the first 30 minutes of the heat treatment. Furthermore, the impact of temperature was investigated by carrying out the treatment at three temperature levels: 290, 295 and 300 °C. The comparison of the heat treated CNCs for different periods of time and at different temperature is shown in Figure 2.

The AFM images comparison visually demonstrated the course of CNCs thermal degradation on TiO_2 (Figure 2). In addition, the impact of temperature on the rate of degradation is evident. The CNCs treated at 300 °C were completely degraded within 30 minutes. In fact, the degradation was completed in 20 minutes (image not shown). Similar pattern was observed for the CNCs exposed to 295 °C. The degradation was also completed within 30 minutes. The rate of CNC degradation at 290 °C is visibly lower, and some CNCs are visible after 30 minutes of the treatment. The complete CNC degradation at this temperature was complete within 45 minutes. The entire set of AFM images depicting the thermal degradation of CNCs at 290 °C is shown in Figure 3.

Significant degradation of the CNCs is clearly visible already after 10 minutes of the treatment, particularly at higher temperatures. Overall, the impact of the temperature on the degradation in the first 10 minutes of the heat treatment is most evident. In addition to the visual comparison, all AFM images were analyzed with Scanning probe image processor (SPIP). Using the software the amount of crystals and overall coverage were determined. Results of these analyses are shown in Figures 4 and 5.

The comparison of the amounts of crystals remaining after the treatments as well as overall coverage of the scanned surfaces quantified the impact of temperature on the CNCs degradation (Figures 4 and 5). The shape of the curves hint toward first order kinetics but within this short set of data we refrain from further speculation. More experiments and data points are required for proper kinetic analysis. However the impact of the treatment temperature was confirmed with the quantification.

The dimensional analysis of the CNCs in the course of the thermal degradation was carried out by determining the change in length of the crystallites. The length of the crystallites is more indicative of the changes due to the high aspect ratio and it is thus not being affected by the AFM tip

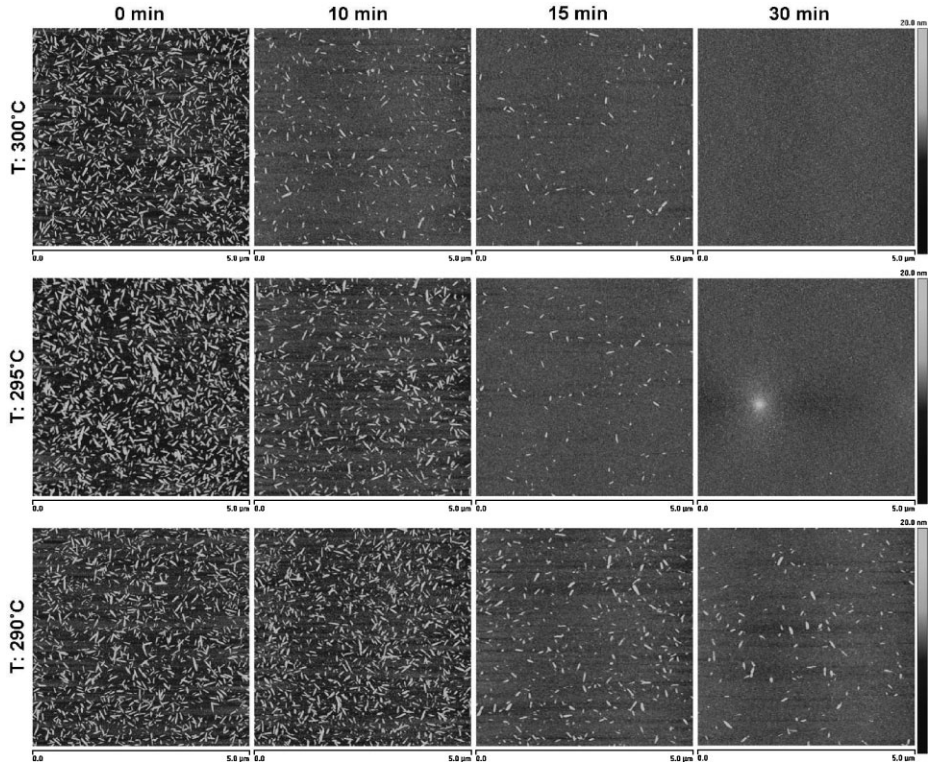

Figure 2.
Comparison of AFM height images of heat treated CNCs deposited on titania surface. Surfaces treated at 290, 295 and 300 °C for different length of time.

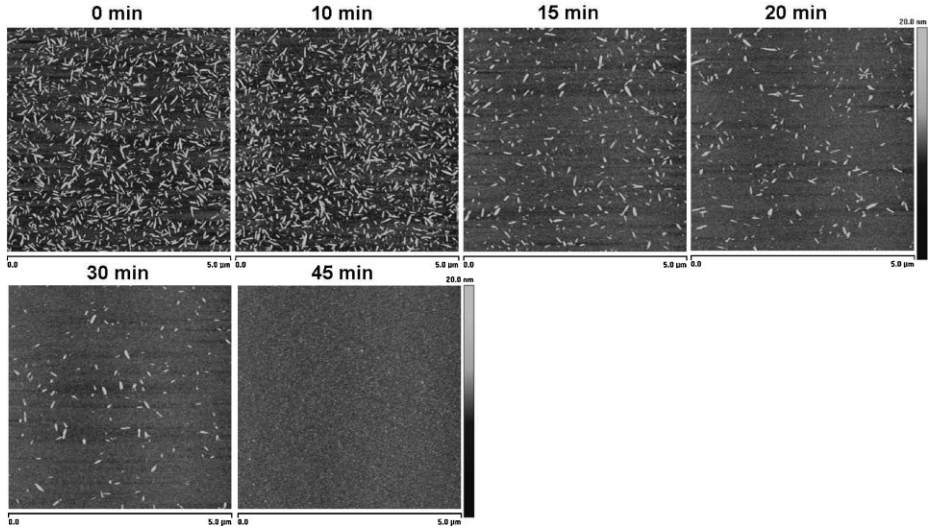

Figure 3.
Comparison of AFM height images of CNCs deposited on titania surface heat treated at 290 °C for different length of time.

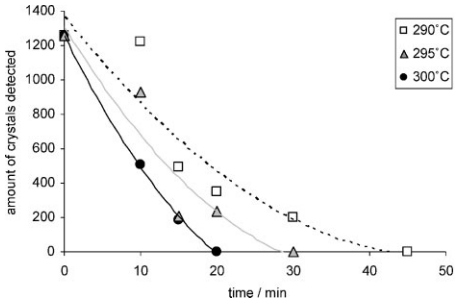

Figure 4.
Amount of crystals as detected by SPIP from AFM images. Comparison of CNC surfaces treated at 290, 295 and 300 °C for different length of time.

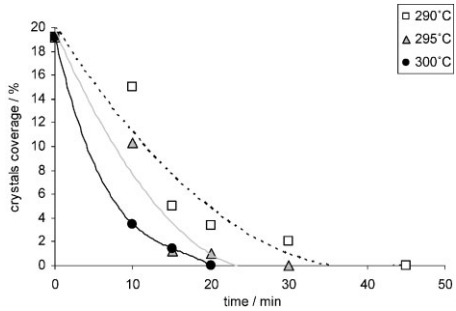

Figure 5.
Crystal coverage as detected by SPIP from AFM images. Comparison of CNC surfaces treated at 290, 295 and 300 °C for different length of time.

exaggeration.[17] The results of CNC length analysis are shown in Table 1.

The impact of temperature on the degradation of CNCs is evident when comparing the change in length after the first 10 minutes of the treatment. Further degradation, however does not follow similar trends. The length of the crystals did not change after 15 minutes treatments at 290 °C, while a steady decreasing trend is observed for the samples treated at 295 °C. The length of the CNCs did not change after 10 minutes of treatment at 300 °C. To confirm or refute these discrepancies in trends, further analysis and more data are required.

Conclusion

Visual analysis of thermal treatment of cellulose nanocrystals (CNCs) deposited on solid surfaces showed different degradation patterns for the CNCs deposited on nano-sized film of amorphous cellulose and on the TiO_2 surface. The CNCs deposited on titania substrate exhibited rapid rate of degradation by being completely degraded within 20 minutes of treatment at 300 °C. The CNCs deposited on amorphous cellulose exhibited markedly slower overall degradation rate, and CNCs were still visible after 120 minutes of exposure to 300 °C.

Visual comparison and analysis of the AFM images clearly demonstrated the impact of temperature on degradation rate of the nanocrystals deposited on TiO_2 substrate in the temperature range of 290 and 300 °C.

The difference of the degradation rate on the two selected substrates is remarkable and it can most probably be attributed to the catalytic activity of TiO_2 in oxidation reactions. Alternate substrates for CNC deposition need to be explored to properly evaluate the impact of amorphous cellulose

Table 1.
Average length and standard deviation in length of CNCs heat treated at different temperatures for different lengths of time.

	290 °C		295 °C		300 °C	
Time	Average	Std. deviation	Average	Std. deviation	Average	Std. deviation
min.	nm	nm	nm	nm	nm	nm
0	103.3	83.8	103.3	83.8	103.3	83.8
10	89.7	73.8	86.6	66.8	65.0	49.7
15	78.2	56.4	55.9	46.2	68.3	48.0
20	78.5	60.0	45.9	41.0		
30	78.8	53.4				

and catalytic activity of TiO_2 on thermal degradation of CNCs.

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