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Abstract:

A simple, solvent-free and low cost method to activate the surface of nanofibrillated cellulose films for further functionalization is presented. The method is based on the oxidative properties of UV radiation and ozone, to effectively remove contaminants from nanocellulosic surface, which remains clean and reactive for at least a week. The efficiency of the method is demonstrated by X-ray photoelectron spectroscopy and contact angle measurements. In clear contrast to previous results on nanoscaled cellulose the relative atomic concentration of non-cellulosic carbon atoms was only 4%, and water completely wetted the surface within seconds. After activation, neither chemical degradation nor morphological changes on cellulose were observed. This surface activation is essential for further functionalization of the film in dry state or nonpolar media. The surface activation was confirmed by silylation and a four times higher degree of substitution was achieved on the activated sample compared to non-activated reference film, as monitored with XPS.

KEY WORDS: microfibrillated cellulose, ozonation, film, cleaning, UV

Introduction

Cellulose is a natural polymer and an almost unlimited source for sustainable production of materials on industrial scale. Recently the interest for nano-scaled cellulosic materials, like nanofibrillated cellulose (cellulose nanofibrils, NFC) or cellulose whiskers (cellulose nanocrystals, CNC) has increased exponentially (Habibi et al. 2010, Klemm et al. 2011, Nishiyama et al. 2008, Walther et al. 2010). The main reasons for the growing interest in nanocellulose are the development of energy efficient and up-scalable production methods (Pääkkö et al. 2007, Saito et al. 2007, Wågberg et al. 2008) and the
extraordinary properties of this renewable material (Eichhorn et al. 2010).

Due to the large surface area and enhanced hydrogen bonding ability of the fibrils, NFC forms strong hydrogels at very low solids content. Furthermore, upon drying the nanofibrillar network in these hydrogels has a high inherent tendency to form film-like structures which is especially interesting feature when considering novel application areas. NFC films are strong, they exhibit low oxygen permeability and they can appear as transparent or translucent plastic-like materials rendering them as an attractive alternative to petroleum-based polymers for example in packaging applications (Lavoine et al. 2012). Moreover, we have developed relatively fast and up-scalable methods to prepare NFC films (Österberg et al. 2013, Peresin et al. 2012, Tammelin et al. 2011) which can be further surface modified e.g. in aqueous media (Orelma et al. 2012).

Nevertheless, the unique properties of NFC hydrogels change dramatically and often unpredictably upon drying or when exposed to nonpolar media. This is why most literature report on application or modification of NFC in never-dried form (Klemm et al. 2011). In our recent paper we proposed that this is due to the carbonaceous contamination layers that accumulates on the surface of highly hydrophilic cellulosic nanofibrils and nanofibrillar films whenever exposed to nonpolar media, e.g. upon drying (Johansson et al. 2011). The passivation layer impedes modification or application based on interactions with the hydroxyl groups of cellulose, via occupying significant part of these groups so that they are no longer available for further functionalization. However, we also found that using appropriate solvent exchange procedure before drying of the NFC dispersion, the irreversible passivation of the surface was avoided and the surface of the individual nanofibrils were highly accessible for further functionalization (Johansson et al. 2011).

The remaining challenge is consequently how to re-activate dry nanocellulosic surfaces. In this contribution we introduce a solvent-free method, to clean and re-activate the NFC film surface, based on the combination of UV and ozone. Ozone is a powerful oxidation reagent used in many applications for
removal of organic contaminants from various surfaces like steel (Kumar and Biswas 2011), sensor ceramics (Chen et al. 2007, Zhang et al. 2006), and atomic force microscopy (AFM) probes (French et al. 2008). UV radiation in the presence of ozone (UV/O\textsubscript{3}) was also found to be the most efficient cleaning method in recycling gold nanoparticle junction arrays (French et al. 2008). Patterned superhydrophilic arrays have also been obtained by UV/O\textsubscript{3} treatment (Luz et al. 2011).

The effect of UV/O\textsubscript{3} on the surface properties of dry films of nanofibrillated cellulose was evaluated with atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS), contact angle (CA) and FT-IR experiments. The enhanced reactivity and accessibility of the hydroxyl groups on the NFC film surface was verified with a simple and well-known silylation reaction. Significant improvement in the surface reactivity of NFC films was observed upon UV/O\textsubscript{3} activation without any severe changes in nanocellulose structure and chemistry.

Experimental Section

*Nanofibrillated cellulose* was prepared by disintegration of fully bleached never dried hard wood kraft pulp using a high shear Fluidizer (Microfluidics Int. Co, USA). The pulp was washed into sodium form prior to disintegration according to a method introduced by Swerin et al (1990) and passed six times through the fluidizer. This treatment removes excess of salt from the pulp suspension and ensures that only sodium ions are associated with anionic groups on the pulp. No chemical or enzymatic pretreatment was applied and the charge density of the pulp was 0.0065 meq/g as determined by conductometric titration according to Katz et al (1984). The 132 cm\textsuperscript{2} large and around 100 µm thick free-standing NFC films were prepared by over-pressure filtration of a 0.84% dispersion of fibrils followed by hot pressing at 100°C and 1800 Pa (Österberg et al. 2013). Sefar Nitex polyamine fabric was used for filtration and remained with the film during pressing. A commercial *UV ozonator* from Bioforce Nanosciences was used to activate the NFC film surface. The nominal power of the UV source
was 80 W, the intensities of the most important wavelengths were 199 for 185 nm and 3975 for 254 nm according to the manufacturer. The distance between sample and radiation source was 2.5 cm. Treatment time for the films was 10 min. The sample size was about 2×4cm.

Efficiency of the activation of the film surface was demonstrated by a simple silylation reaction performed on films obtained in pilot scale, according to Tammelin et al (2011) and Peresin et al (2012). The modification protocol is a slight variation of the method used to modify nanofibrils in bulk (Johansson et al. 2011). Films of about 100 mg were submerged in 150 ml Dimethylacetamide (DMA, 99% - Sigma-Aldrich) in a reaction vessel under continuous Nitrogen flow to evacuate any remaining oxygen. The film was kept in DMA under magnetic agitation until the temperature reached 80 °C. Hexamethyldisilazan, (> 99 % purchased from Sigma-Aldrich) was added drop-wise while stirring (1 μl reagent/mg of film). Reaction was continued over night at constant temperature. Films were thoroughly washed with DMA and with methanol (HPLC grade; Rathburn) to remove any possible unreacted chemicals. Finally, the films were allowed to dry in air.

X-ray photoelectron spectroscopy, XPS (Kratos Analytical AXIS 165 electron spectrometer with monochromatic A1 Kα irradiation at 100 W), was used for surface chemical analysis of the free-standing NFC films. More specifically the effect of UV/O₃ treatment and silylation on surface chemical composition was monitored. The measurement procedures and acquisition parameters were optimized for cellulosic samples as described by Johansson (Johansson 2002). Samples were analysed after one week storage in desiccator. A minimum of three different areas were measured per sample.

AFM (Nanoscope IIIa scanning probe instrument from Digital Instruments, Santa Barbara, USA) was used to probe the surface topography of the films before and after UV/O₃ treatment. Three different areas on each sample were scanned in tapping mode in air using silicon cantilevers (SCD 15/AIBS, MicroMasch, Talinn, Estonia). The nominal resonance frequency of the cantilevers was around 300 kHz.
Contact angle measurements: The sessile drop method was employed for determination of water contact angle with a video camera based fully computer-controlled contact angle meter (CAM 200 from KSV Instruments Ltd., Finland). The measurements were performed at room temperature using deionized water further purified through a Milli-Q water purification unit. At least five separate measurements were made for each sample either 15 min. or 1 week after UV/O<br>3 treatment. The samples were stored in a desiccator prior to measurements.

Fourier transform infrared spectroscopy (FTIR) was applied to verify that no chemical degradation of the cellulose occur during the UV/ozone treatment. With the BIO-RAD UMA 500 spectrometer (USA) equipped with a universal attenuated total reflection (ATR) germanium crystal the films could be analyzed directly without further sample preparation, the analysis depth being about one micrometer. The spectral data was processed with GRAMS AI software (Thermo Scientific, Galactic Industries Corporation, New Hampshire, USA. All spectra were baseline-corrected and further normalized to have the same value at 1200 cm\(^{-1}\). An average spectrum of three measurements is reported.

Results and Discussion

UV ozone treatment was evaluated as a method to clean the surface of NFC films. The method is based on the power of ozone to decompose small molecular weight organic substances while not affecting the cellulosic structure. UV light generates free radicals on the surface of low molecular weight polymers leading to oxidative degradation. UV radiation (185 nm) reacts with atmospheric oxygen and forms atomic oxygen and ozone, both strong oxidizers. Ozone absorbs the 254 nm UV radiation and dissociates into molecular oxygen and atomic oxygen (Zhang et al. 2006). UV light excites ambient oxygen molecules from their ground spin-triplet state into a spin-singlet state thus creating a more reactive environment in which the immediate cleavage of organic bonds like C-C, C-H
and O-H into volatile organics takes place (Ye et al. 2005). This procedure has been found to be more efficient than UV radiation or ozone treatment separately.

NFC films were prepared by overpressure filtration of native unmodified NFC (Österberg et al. 2013). After hot pressing, a strong, dense and translucent film was obtained within a couple of hours (Fig. 1a). The density of the film is about 1250 kg/m$^3$ (Österberg et al. 2013). XPS wide spectra were recorded to confirm that the NFC film does not adsorb any foreign chemicals from the fabric during pressing. Only carbon and oxygen signals were observed (Online resources 1). The film was then treated with ozone created by UV light in a commercial UV ozonator, thus removing much of the organic airborne contaminants from the surface.

**Fig. 1** a) Free-standing translucent NFC film with the diameter of 13 cm. In the inset an AFM topography image of a 9 µm$^2$ area of the film surface is shown. b) XPS C 1s high resolution regions of untreated film (blue lower spectrum) and UV/O$_3$ treated film (red upper spectrum). The measurements were done one week after treatment. Observe the reduction in the C-C carbon. c) Corresponding water contact angle values for untreated reference (blue squares), UV/O$_3$ treated after 15 min (unfilled red triangles) and after one week (red filled triangles). Note that due to the rapid spreading of the water droplet only a few measurement points close to 0s are visible 15 min after treatment.

The surface topography of the film was homogeneous and with only nanometer scaled roughness, as seen in the AFM image in the inset of Fig. 1a). In our previous work, we demonstrated that although pure and reactive when dispersed in aqueous media, NFC easily accumulates substantial amount of non-cellulosic material upon drying which passivates the fibril surfaces (Johansson et al. 2011). Experimental evidence of such behavior was obtained by X-ray photoelectron spectroscopy (XPS). A high amount of carbon atoms which are bonded only to other carbon or hydrogen atoms (C-C carbon signal) was observed at the outmost surface of the nanofibrillated cellulose. Similar behaviour was observed in the case of untreated film surface (Fig. 1b). The relative abundance of C-C carbon was
approximately 11 % for the untreated nanocellulose films which is comparable to the previously reported results for nanocellulosic fibrils (Andresen et al. 2007, Littunen et al. 2011, Uschanov et al. 2011). Similar trend was perceived in the case of water contact angle values (Fig. 1c). The contact angle for untreated film was around 30° in correlation with our previous findings, indicating the presence of a passivation layer on the film surface. Nevertheless, after treating the sample with UV/O₃ for ten minutes, the hydrophilicity of the sample increased and the water droplet completely wetted the surface within a few seconds. Simultaneously the C-C carbon signal decreased to 4%, a very low value for nano-scaled cellulose samples and a 36% decrease as compared to untreated sample.

It is worth noting that the surface remained very hydrophilic for at least one week after the UV/O₃ treatment, as evidenced by contact angle values (Fig. 1c), suggesting that passivation of this surface after UV/O₃ treatment is very slow. This behavior is the opposite to the one observed for most mineral surfaces. After the same cleaning procedure, silica surfaces are extremely reactive. However, they accumulate airborne contaminants within minutes when kept in ambient air. We suggest that the unique behavior observed for cellulosic substrates is due to the amphiphilic character of the cellulose molecule and its ability to rearrange the outermost surface molecules, hence minimizing its surface free energy. This behavior may well be one reason for the overall stability of cellulose materials (Johansson et al. 2011, Johansson et al. 2012). The rearrangement at the surface is reversible and thus, the cellulose is fully reactive when immersed in aqueous media where the hydrophilic plane of the cellulose molecules adapts to the hydrophilic media. It must be noted that although the NFC film was made from nanofibrils, after the film formation and drying, it can be compared to macroscopic cellulose samples like filter paper or wood fibres. During the drying process, hydrogen bonds are formed between fibrils and although there is no evidence of increase in crystallinity, during the pressing the films become very dense (Österberg et al. 2013). If, on the other hand, the same treatment is conducted on nano-scaled ultrathin films of dispersed NFC fibrils, the same hydrophilicity and cleanliness is achieved but the film is considerably more reactive and accumulates a passivation layer over time (results not shown). The
ultrathin film is more porous and thus has higher surface area, thus being less stable than macroscopic cellulose films.

The effect of UV/O$_3$ treatment on activation of the surface was corroborated by means of a simple surface reaction. Chemical modification through silylation chemistry was performed directly on the surface of the dense NFC film before and after exposing the film surface to the UV/O$_3$ treatment. The results of the reaction were evaluated by XPS analysis. XPS high resolution spectra for carbon (C1s) and silicon (Si2p) are shown in Fig. 2.

**Fig. 2** XPS C 1s and Si 2p high resolution regions of untreated film (blue bottom spectrum), untreated and silylated film (black middle spectrum) and UV/O$_3$ activated and silylated film (red upper spectrum).

In the high resolution carbon 1s spectra no clear differences between unmodified (blue) and silylated unactivated film is observed. However an increase in the peak around 284 eV is observed for the activated and silylated sample. In this region both C-C bonds and C-Si bonds appear. In the high resolution Si 2p spectra the effect of surface activation is clearly seen. A small increase in the Si band is observed for the silylated unmodified sample (black spectrum) but the increase is much higher for the activated and silylated sample (red spectrum). The degree of substitution was calculated based on the relative amount of silicon on the surface and was 0.07 for un-activated and 0.26 for UV/O$_3$-activated sample, corresponding to a four-fold increase in surface activity due to the UV/O$_3$ treatment. From the wide spectra and high resolution oxygen 1s spectra for the respective samples (Online resource 2 in electronic online resources) we conclude that no significant chemical change except the silylation reaction is occurring at the surface.

The oxidative reaction induced by ozone is very strong, introducing carboxylic acid or carbonyl groups at the surface, and leading to severe degradation of low molecular weight polymeric substrates like rubber or low density polyethene (Hedenberg and Gatenholm 1996, Romero-Sánchez et al. 2005),
There is no available literature on the effect of ozone on NFC, although ozone is commonly used in chlorine free delignification of pulp in the papermaking industry (Katz and Scallan 1983). Koljonen et al. (Koljonen et al. 2003) demonstrated that the ozone oxidizes lignin on the pulp fibre surface, which is seen as a decrease in C-C carbon (present in lignin) and increase in the O–C=O carbon in XPS data. Yet, AFM imaging revealed that the cellulose microfibrils stayed intact during the ozone treatment. Ozonation has moreover been used to increase the adhesion between low density polyethene and cellulose fibres in composites (Hedenberg and Gatenholm 1996, Kurosu et al. 2009). As expected, while ozone treatment of polyethene was proven to be efficient ozone treatment of cellulosic fibres decreased the overall adhesion. In photochemical bleaching of pulp (Ohtsuki et al. 2011) or wood powder (Kurosu et al. 2009) the power of UV/O\textsubscript{3} treatment is utilized to remove lignin without decreasing the strength of the pulp (Kurosu et al. 2009). To ensure that there was no degradation occurring at the NFC film surface due to the oxidation, the films were imaged with AFM before and after treatment and the chemical composition of the film was evaluated using attenuated total reflection (ATR) IR (Fig. 3).

Fig. 3 a) AFM topography images, and b) one representative line scan for untreated NFC free-standing film (NFC reference, left) and NFC film that have been UV/O\textsubscript{3} treated (right). c) ATR IR spectra for the two samples illustrate that the sample is not chemically modified due to the ozonation. The area of dashed rectangle from 2000-1200 cm\textsuperscript{-1} is shown magnified in the inset. Since the spectra overlap the UV/O\textsubscript{3} spectrum was shifted up by 1 a.u. in the inset to facilitate comparison (the upper curve corresponds to UV/O\textsubscript{3} treated sample).

From the AFM topography images (Fig. 3a) and the representative lines scans (Fig. 3b) it is obvious that the fibrillar structure was maintained and there is no evidence of changes in the fibril width that would indicate degradation although a decrease in molecular weight cannot be excluded based on these results. The carbonyl groups are very IR active and are usually seen in ozone treated polymer films in the 1700-1750 cm\textsuperscript{-1} region although the reaction is taking place at the surface (Hedenberg and...
However, as seen in the magnification of this region there are absolutely no changes of the ATR IR spectra for the film before and after UV/O$_3$ treatment. As a matter of fact no chemical changes are observed in the spectra. We further note that the carbon peak in XPS spectra (Fig. 1b) is well resolved and there are no significant changes occurring in the C4 region suggesting that the surface retains its chemical structure. This is in contrast to e.g. oxygen plasma treatment of cellulose fibres, where quite short treatment times induces clear degradation, observed as increase in C–C carbon and oxidation, observed as an increase in O–C=O carbon (Carlsson and Ström 1991).

The plastic-like nanocellulosic films can be seen as an emerging application area due to film’s peculiar features: the strong self-association tendency of nanofibrils during drying creates smooth, strong, dense, flexible, transparent/translucent films with low transmission rates of gas molecules also at humid conditions (Österberg et al. 2013, Sehaqui et al. 2011). Recently it has been shown that the film manufacturing technology is up-scalable in order to produce films using industrially relevant roll-to-roll technique (Tammelin et al. 2011). For optimum performance and in order to create functional materials there is a need to modify the surface by chemical reactions. Therefore a simple, solvent-free cleaning method, such as the one presented here, should be highly beneficial to boost the film surface reactivity for further functionalizations, eliminating one of the obstacles hindering industrial applications of NFC.

**Conclusions**

A simple solvent-free method to clean and activate the NFC film surface was demonstrated. The method based on UV/O$_3$ treatment enhanced significantly the reactivity and accessibility of the hydroxyl groups on the cellulose surface thus increasing its hydrophilicity and simultaneously facilitating its more efficient functionalization. Almost four times higher degree of silylation was achieved on activated NFC films. Additionally, the effect was observed to be long-lasting and the treatment did not degrade the cellulose. In this respect cellulose differs from both ceramics and metals that stay clean for only minutes or other organic materials that are degraded by ozone. Due to the recent advances in up-scaling both
NFC production and NFC film manufacturing this simple method, based on a commercial technique, to tailor the surface of the NFC film may have large practical implication.

Electronic Supplementary Material

XPS Wide spectra of untreated NFC film and UV/O₃ treated films before (Online Resource 1) and after (Online Resource 2) silylation are shown in the Electronic Supplementary Material.

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