Journal of Paper Conservation

ISSN: (Print) (Online) Journal homepage: www.tandfonline.com/journals/yjpc20

Degraded Paper: Stabilization and Strengthening Through Nanocellulose Application

Lucy Gmelch, Electra Maria Letizia D'Emilio, Thomas Geiger & Carmen Effner

To cite this article: Lucy Gmelch, Electra Maria Letizia D'Emilio, Thomas Geiger & Carmen Effner (28 Feb 2024): Degraded Paper: Stabilization and Strengthening Through Nanocellulose Application, Journal of Paper Conservation, DOI: 10.1080/18680860.2024.2317831

To link to this article: https://doi.org/10.1080/18680860.2024.2317831

Published online: 28 Feb 2024.

JOURNAL OF PAPER CONSERVATION
https://doi.org/10.1080/18680860.2024.2317831

RESEARCH ARTICLE
OPEN ACCESS
Check for updates

Degraded Paper: Stabilization and Strengthening Through Nanocellulose Application

Lucy Gmelch [a], Electra Maria Letizia D'Emilio [a], Thomas Geiger [b] and Carmen Effner [a]

[a]Berner Fachhochschule, Hochschule der Künste Bern, Institut Materialität in Kunst und Kultur, Bern, Switzerland; [b]Laboratory for Cellulose & Wood Materials, Empa – Swiss Federal Laboratories for Materials Science and Technology, Duebendorf, Switzerland

ABSTRACT
Cellulose nanomaterials are a promising material for the stabilization of degraded paper, since their characteristics in composition, structure and physical properties are close to those of cellulose. Two types of nanocellulose were tested regarding their performance in stabilizing fragile papers: cellulose nanofibrils (CNF) and cellulose nanocrystals (CNC). The suspensions were applied to a pure cellulose paper and historical newspaper. The study included optical and microscopic characterization, determination of pH, conductivity, and rheology as well as measurement of changes in tensile strength after treatment. The results showed that the pH, as well as the optical and haptic properties, were not altered after treatment. A 50% increase in paper's tensile strength is achieved with 3% CNC applied on the paper. In addition, fluorescence microscopy demonstrated that, due to their nanoscale dimension, the suspensions can reinforce the surface but also fully penetrate the paper matrix achieving therefore an overall stabilization.

KEYWORDS
Nanocellulose; cellulose nanomaterial; paper stabilization; mechanical testing; fluorescence microscopy

ZUSAMMENFASSUNG
Cellulose Nanomaterialien sind ein vielversprechendes Material für die Stabilisierung von degradiertem Papier, da sie in Zusammensetzung und Struktur der Cellulose ähnlich sind. Cellulose Nanofibrillen und Cellulose Nanokristalle wurden in Hinblick auf ihre Fähigkeit zur Stabilisierung von fragilen Papieren getestet. Die Suspensionen wurden auf Filterpapier und historisches Zeitungspapier aufgebracht. Die Charakterisierung der Proben beinhaltete optische und mikroskopische Veränderungen, Messung der Zugfestigkeit und Bestimmung des pH-Werts. Die optischen und haptischen Veränderungen der Papierproben durch die Behandlung waren minimal, der pH-Wert wurde nicht negativ verändert. Die Papierfestigkeit wurde – bei einem Auftrag von 3 wt% Nanokristallen – um 50% erhöht. Mittels Fluoreszenzmikroskopie konnte gezeigt werden, dass die Suspensionen aufgrund ihrer Dimensionen im Nanobereich sowohl die Oberfläche verstärken als auch das Papierfasergefüge durchdringen und somit eine umfassende Festigung erzielen.

SCHLÜSSELWÖRTER
Nanocellulose; Cellulose Nanomaterialien; Papierstabilisierung; Zugversuche; Fluoreszenzmikroskopie

Introduction

The depolymerization of cellulose in historical documents is caused by several decay processes which in turn may lead to irreversible degradation and the ultimate loss of valuable information. In particular, papers produced between 1850 and 1950 have a short life span due to their mechanical pulp content (see Figure 1). The high proportion of short wood fibres makes the paper very unstable and the acid content in the paper accelerates the degradation process by acidic hydrolysis. Furthermore, depolymerization of the cellulose can occur due to mould or ink corrosion, as both can act as additional acid suppliers. Combined with inadequate storage conditions and frequent use, damaged paper can degrade to the point of total disintegration. Documents of historical value are irretrievably lost. Brittle and fragile papers are particularly susceptible and at risk of further damage by the stress caused through handling the objects and therefore need to be stabilized.

A common method of paper stabilization is to line it with Japanese paper. Adhesives such as starch paste, or cellulose ether are applied with a brush to the lightweight Japanese paper or the original object. The two papers are subsequently glued together and dried between blotters. The physical integrity of the reinforced paper is preserved, and the aesthetic unity restored. However, the fibres of the Japanese paper are visible, at least in the printed areas, and result in a cloudy appearance by reducing the overall contrast of the paper.

In recent years, various approaches for the use of cellulose nanomaterials (CN) as a new and promising

CONTACT Lucy Gmelch lucyjohanna.gmelch@hkb.bfh.ch Hochschule der Künste Bern, Fellerstrasse 11, Bern 3027, Switzerland

Figure 1. Brittle and fragile historical paper from mechanical wood pulp breaks and crumbles into pieces when wrinkled.

material for stabilization of paper were discussed: Their application as films for the mending of tears (Harwood, 2011; Dreyfuss-Deseigne, 2017), as sheets for reinforcement (Santos et al., 2016a and 2016b) or as nanocellulose pulp for filling lacunae (Camargos et al., 2017). Völkel et al. (2017) showed that the consolidation of weakened paper can be achieved by the application of a nanocellulose suspension without the use of an additional adhesive. They used two different types of CN, a bacterial cellulose and cellulose nanofibrils, which were tested regarding their performance in stabilizing fragile papers. The treatment did not affect the optical and haptic properties and no negative effect on cellulose integrity could be observed after accelerated aging. Regarding paper stability however, the data obtained from long and zero span measurements were scattered without providing consistent trends. In a more recent study, the research team sprayed aqueous cellulose nanofibrils suspensions onto heat-damaged papers using an airbrush (Völkel et al., 2022). The stabilization performance was determined by individual bending tests. The treatment was able to mechanically stabilize the material and did not negatively impair visual appearance and legibility in the visible and IR ranges.

The present study aims to further investigate the use of nanocellulose in paper conservation by proposing an application of cellulose nanofibrils (CNF) and cellulose nanocrystals (CNC). CNC has not been used in the form of suspensions for the stabilization of paper while this study was being carried out. In the meantime, in a PhD research defended in 2022 the use of both CNF and CNC suspensions have been tested, separately and mixed, for the stabilization and strengthening of traditional handmade rag paper damaged by fire (Zanetti, 2022) and other studies were published on the influence of CNC on paper reinforcement (Operamolla et al., 2021; Perdoch et al., 2022). Moreover, Operamolla et al. (2021) have shown a way to remove a consolidation treatment with nanocrystalline cellulose on paper, demonstrating reversibility.

CNC is thought to be composed of the elementary structural unit of cellulose fibres and represents the crystalline region of individual cellulose chains, held together by hydrogen bonding (O'Connor et al., 2014: 226). In this research, a CNC type with the trade name NCC^{TM} was used, which is produced by the Canadian company CelluForce (Montreal, Canada). The CNC have unique properties such as high aspect ratio, high surface area and high mechanical strength such as CN in general, indicating that they will successfully penetrate into the substrate matrix and strengthen the depolymerized historical artifacts. In contrast to the filamentous CNF, it is expected that the crystalline CNC could form less of a fibre network on the surface of the paper than penetrate into the interfibrillar regions of the paper structure. Their production methods via strong acid hydrolysis are a simple methodology, resulting in an environmentally friendly material that is produced on a large scale and therefore easily accessible at a low cost (Shankaran, 2018). Currently, there are no specific regulatory occupational exposure limits (OELs) established for engineered nanomaterials including CN (see Appendix: *Recommended health* *and safety measures for working with nanocellulose materials*). Another important aspect is that, like the papers to be treated, the crystals are primarily made of cellulose and thus chemical and physical compatibility with the substrate is expected to be achieved with the treatment. In terms of solvent compatibility, CNC are basically hydrophilic; however, they can be suspended in a mixture of alcohol and water which further reduces the risk of swelling of the substrate. Due to their size and structure, it is expected that the crystals penetrate the cellulose structure of the substrate and significantly increase the strength of the paper.

The main questions addressed in this paper are:

- Are suspensions with CNF and CNC suitable for the treatment of destabilized paper?
- How do they effect the stability of the paper as well as other properties (colour, pH, structure)?
- What are the differences between the use of CNF and CNC?
- Is it possible to use a combination of CNF and CNC for even better results in paper strength?

Experimental

Materials

Paper samples

Papers chosen for treatment were Whatman® no.1 filter paper (HUBERLAB. AG, Switzerland) and naturally aged newsprint paper. The newsprint paper dates from around 1870. It is machine-made and consists of mechanical wood pulp with internal sizing, probably an acidic sizing with resin and alum. The newspaper is printed with black ink, which probably contains carbon black and oil. Sizing and printing ink were not examined in detail. Certainly, the penetration of the nanocellulose at the printed areas is different from the paper without printing ink, but no optical or mechanical differences between printed and unprinted areas after treatment were found in the tests carried out. Whatman® no.1 filter paper is made from alpha cellulose using high quality cotton linters. It is used for analytical purposes because of its high homogeneity.

Nanocellulose

The raw material source for CN is delignified cellulose, which is broken down by hydrolysis. Therefore, its composition and structure are basically the same as cellulose. Cellulose particles with at least one dimension on nano-level (1–100 nm) are considered as CN. Depending on the manufacturing process, a distinction is made between cellulose nanofibrils (CNF), cellulose nanocrystals (CNC), bacterial cellulose (BC) and electro spun nanocellulose fibres (ECNF). CNF and CNC are being obtained by mechanical or chemical breaking down of cellulose fibres in particles in nano dimensions, while BC and ECNF are being obtained by a build-up of nanofibers from low molecular sugars from bacteria or from dissolved cellulose by electrospinning.

CNF was obtained from the Swiss Federal Laboratories for Materials Science and Technology, Empa (Duebendorf, Switzerland). According to REM analysis the length of a fibril between its network nodes is estimated at up to 1 µm with a width of 20–100 nm. The fibrils were received as a 2 and 8 wt% suspension in deionized water.

The NCC™ CNC (CelluForce) are 50–350 nm long and display a width of 5–20 nm. The crystals were prepared with deionized water as a 6 wt% suspension at Empa. The nanocellulose powder and the water have been blended via two cycles of Speed mixer, respectively 3 min at 1000 RPM and 3 min at 2000rpm. The subsequent degassing was performed through one mixing cycle of 3 min at 80 Bar and 800 RPM. To help the clumps removal three ceramic milling balls with ø 1 cm were used.

Rhodamine B-isothiocyanat (RBITC) (Merck KGaA, Germany), mixed with distilled water and Sodium Hydroxide Flakes 98% (Alfa Aesar by Thermo Fisher Scientific, Germany), was used to dye the CNs.

Methods

Production of raw materials

According to the literature cellulose nanocrystals are produced by acid hydrolysis with sulfuric acid. The amorphic cellulosic parts of the cellulose stain are dissolved from the polymer matrix under strongly acidic hydrolysis conditions in an aqueous matrix, thus releasing nanocrystals into the aqueous solution. The use of sulfuric acid imparts stability to the CNC in aqueous solutions due to electrostatic repulsion resulting from the addition of negatively charged acidic sulfate ester groups on the surface of the crystals. After hydrolysis, CNC is neutralized by sodium hydroxide (NaOH) to remove free acid residues and is mechanically dispersed to form aqueous colloidal gels (Revol et al., 1992: 171; Dufresne, 2020).

CNF suspensions at a solid contend of 2 wt% were obtained from elemental chlorine-free pulp (ECF from Mercer Stendal, Zellstoff Stendal GmbH, Arneburg, Germany). The pulp was disintegrated by using an ultra-fine friction grinder (supermass-colloider MKZA10-20 J CE, Masuko Sangyo Co., Ltd., Kawaguchi/Saitama, Japan) with an energy input of 9 kWh/kgpulp. Subsequently, the aqueous suspensions were dewatered under pressure to 10.6 wt%.

Preparation of suspensions

The initial suspensions were diluted with deionized water to 0.5, 1, 2 and 3 wt% CNF/CNC each. A second set of suspensions was diluted with water and ethanol to 0.5, 1, 2 and 3 wt% CNF/CNC each with an ethanol content of 33%. Additionally, a combined suspension with 3 wt% CNC and 0.5 wt% CNF in water was prepared. During processing, the suspensions were agitated with a magnetic stirrer.

Paper samples

Paper samples were cut into sheets of 14 × 32 cm for application with film applicator. After application, 6 strips 15 mm wide and 18 cm long were cut out of each sheet for the mechanical tests. Two sheets per set were prepared to have sufficient strips for the mechanical test, in which 10 strips per set were tested. A total of 20 sets of Whatman® no.1 filter paper and 25 sets of newsprint paper were prepared and examined. For pH measurement, 6 sheets Whatman paper 14 × 32 cm were prepared, two sheets each with a 3% suspension of CNC and CNF as well as two for reference to have sufficient material available for a double determination with 2 g paper each. No pH determination was carried out on the newsprint paper. For visual and haptic characterization, small fields of approx. 5 × 7 cm on a newsprint paper sheet of 14 × 32 cm were treated with a brush. The paper samples were preconditioned at 80% RH in a cedar wood tray (GMW, Germany) for 12 h before application of the nano cellulosic suspensions to reduce surface tension and improve wettability. Preliminary tests have shown that preconditioning the papers leads to better penetration of the treatment suspensions. There were practical reasons for preconditioning for 12 h, as the papers could be placed in the humidification chamber the day before and treatment could be started directly the next morning. A shorter preconditioning period of 1–2 h would probably also be sufficient.

Application

The different types of CN were applied to the paper samples by brush for visual and haptic characterization and with a film applicator (Figure 2) for the other analysis. The brush application corresponds to a conservation treatment on a historical object. The use of a film applicator leads to a more uniform application, which is required for analytical purposes.

Application by brush was carried out by full coating with a polyester brush 15 mm wide with horizontally strokes on the suction table to quickly reduce the water content. Application with a film applicator was carried out by full coating in a thickness of 200 µm on the suction table. The amount of the CNs applied with film applicator was determined for all samples. Subsequently, the samples were dried in a dry stack between a pair of very fine and smooth woven polyester fleece (Viledon®, GMW, Germany) and blotting paper for at least 12 h.

Figure 2. Application of nano cellulosic suspension on historical newspaper with a film applicator.

Fluorescence Labelling

The penetration of the nanocrystals into the substrate was investigated through labelling. CNC was linked chemically to Rhodamine B-isothiocyanate (RBITC) as descripted in the protocol proposed by Nielsen et al. (2010). The CNC (833.3 mg) was individually suspended in 200 mL of 0.1 M natrium hydroxide along with 25 mg of RBITC and stirred for 4.5 days in the dark at 70 °C in an oil bath. The suspension was centrifuged (15 min, 6000 rpm) and the orange supernatant discarded. The precipitate was washed with 0.1 M natrium hydroxide (4 × 40 mL) aqueous solution and dialyzed in a dialysis membrane (MWCO:6-8kD) for 1 month at a 12 h exchange rate in a 10 L vessel of deionized water. Then, the suspensions were freeze dried for 1 week at 4.6×10^{-2} mbar. The dialysis was controlled by thin layer chromatography (TLC) as explained by Soppa et al. (2013). An examination with fluorescence labelling was so far only carried out on Whatman® paper. A drop of 200 µL suspension of 0.5 wt% CNC marked with RBITC was applied with a micropipet on the Whatman® paper, another set was immersed for 30 s in the suspension. Both were left to dry at room temperature for 24 h. The paper was then cut into cross sections using a razor blade.

Table 1. List of standards, technical data, equipment, and suppliers used for analytical methods.

Analytical method	Standard	Technical data	Equipment	Supplier
Microscopy		Jenoptik ProgRes® SpeedXT core 3, Software Jenoptik ProgRes® CapturePro 2.10	Polarization microscope, Filter I3 Blue excitation BP 450–490, Blocking Filter LP 515	Jenoptik AG, Germany
pH of suspensions		pHC101 Electrode	HQd Portable Metre	Hach Lange GmbH, Switzerland
Conductivity of suspensions		CDC401 Electrode	HQd Portable Metre	Hach Lange GmbH, Switzerland
Rheology of suspensions		Physica MCR with a DG26.7 double gap cylinder	Rheometre	Anton Paar Switzerland AG, Switzerland
pH of paper samples	ISO 6588-1: 2012	Metrohm 827 pH lab	pH-metre	Metrohm AG, Switzerland
Tensile strength	EN ISO 1924-2: 2008, EN 20187: 1993	zwickiLine Z 2.5	Tensile testing machine	ZwickRoell GmbH & Co. KG, Germany

Analysis

Table 1 lists the standards, technical data, equipment, and suppliers used for each analytical method.

Visual and haptic characterization

The treated samples were compared with the untreated reference material in a visual (formation of gloss, water edges, agglomerations, or films) and haptic (surface structure, flexibility, tension, thickness) examination.

Gravimetric analysis

The papers were weighed on an analytical balance before and after each treatment, and before preconditioning in a cedar wood tray as described above. Before weighing, the papers were left for three days under controlled climatic conditions (23°C at 50% RH) to ensure comparability.

Fluorescence microscopy

The sections were investigated by polarized microscopy with a filter I3 Blue. The samples were illuminated through CoolLED pE-300 with a blue LED used at 100% of its emission power. The photographic documentation was taken with a digital SLR camera, and the corresponding PC software set with an exposure time of 100 ms. The figures were processed with Adobe Illustrator.

Determination of pH, conductivity, and rheology of suspensions

Conductivity, pH and rheology of the suspensions was determined. Conductivity and pH were measured with an HQd Portable Metre using a pHC101 Electrode (pH) and a CDC401 Electrode (conductivity) at constant temperature of 24°C. The suspensions were produced using Milli-Q water at pH 5.8–6. The pH value of the CNF before dilution was not determined, as measuring the CNF paste with a pH electrode proved to be difficult. The rheological properties of the formulations were analysed with the Physica MCR 300 Rheometer. It was used with a CC27 1158 concentric cylinder for jellified and high viscous system and DG26.7 double gap cylinder for water-like adhesives.

Determination of the pH-value of treated and untreated paper samples

The pH value was only determined on Whatman® paper samples. The measurement of pH was conducted according to standard process ISO 6588-1: 2012 and 2 g of Whatman® no.1 paper untreated and treated with 3 wt% solution of CNF and CNC was extracted for 1 h with 100 ml of cold water of high purity. After filtration, 2 ml of potassium chloride solution (Dr. Grogg Chemie AG, Switzerland) were added, and pH was determined using a pH-metre.

Measurement of tensile strength after folding according to Bansa-Hofer

The measurements of tensile strength were conducted according to standard process EN ISO 1924-2:2008. Treated paper samples and references were equilibrated to 50 +/− 2% humidity at 23 +/− 1°C for 48 h according to the standard method EN 20187:1993. Samples of 15 mm wide strips with a test length of 180 mm were folded on a folding machine (Figure 3) in a standardized manner (Bansa & Hofer, 1980: 352) to create an intended breaking

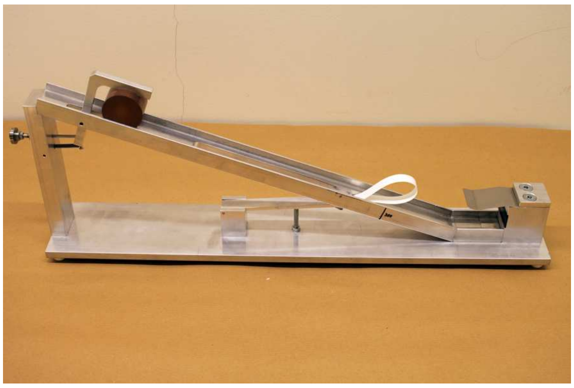


Figure 3. Folding machine used for standardized folding of the paper samples according to Bansa-Hofer.

point. For this purpose, the paper strip was formed into a loop and the ends were fixed together in the device provided. The paper loop was once rolled over by a cylinder of 460 g, which is set in motion on an inclined plane with a gradient of 20%. This creates a standardized fold in the paper strip, which acts as the intended breaking point. Afterwards, the samples were measured in a tensile testing machine (zwickiLine Z2.5, ZwickRoell, Switzerland) with 10 repetitions to minimize paper inhomogeneity. The test parameters are shown in Table 2.

Results and discussion

Cellulose nanofibrils aqueous suspensions with a higher solid content tend to form agglomerations on historical newspaper, while suspensions with a lower solid content created a more uniform application. However, the influence of water increased and led to the formation of water edges on the newspaper if using suspensions with a lower solid content of 0.5 wt% or 1 wt%. Judging by the time the suspension remained visibly wet on the paper surface, the penetration of cellulose nanocrystals was poor compared with cellulose nanofibrils, especially for suspensions with a higher solid content. In general, the application was more difficult for the historical newspaper, due to its hydrophobic character caused by internal sizing and degradation products. The printed areas are especially hydrophobic and tend to worsen penetration.

Suspensions made of CNF and CNC mixed with deionized water and ethanol in ratio 67:33 were also applied. The addition of ethanol resulted in a faster absorption compared to pure water and eliminated the formation of water edges on the historical newspaper. However, the addition of ethanol also enhanced aggregation, especially for CNF, resulting in a less uniform application.

Another set was treated with CNC at the same concentrations but with reduced water content (67:33 water:ethanol) and the papers were additionally premoistened by misting with an ethanol–water-mixture (ratio 30:70). By doing so, the surface tension could be reduced, and the CNC-suspensions absorbed more easily.

The combination of CNF and CNC in a suspension with 3 wt% CNC and 0.5 wt% CNF in water was particularly slow to penetrate, which meant that the coated papers had to remain under suction on the vacuum table for several minutes before they could be put away to dry. It may be possible that the fibrils of CNF, which form a network, hinder the CNC from penetrating further into the paper structure. There may also be interactions between the two types of CNs. Therefore, the two suspensions were applied successively in a further set of samples.

Application with a brush, as would be done in conservation practice on a historical paper to be stabilized, would probably be less homogeneous in terms of film thickness and the effect of the treatment would therefore possibly be somewhat lower than in these experiments.

The pH-value of CNF suspensions from 0.5–3 wt% in water (Table 3) shows an exponential curve's decay and lies between 4.9 and 5.8. The pH decreases exponentially in function of the concentration. Increasing the concentration, the acidity increases. Its behaviour is moderately acidic, due to the deionized water (pH 5.8–6) used for dilution. The pH of CNC suspensions from 0.5–3 wt% in water (Table 3) on the other hand is linear and doesn't show any changes in the pH value at the increase of concentration. It shows a basic tendency with values between 6.6 and 6.8. The absence of a straight line could be due to measurement inaccuracy. The fact that the pH values of the CNC suspension are higher than those of the CNF suspension cannot be explained and would require further analysis. The same deionized water was used for both dilutions.

Table 4 shows the results for conductivity of CNF and CNC suspensions. Both curves scale linearly proportional to the concentration without passing through the origin. The slope of CNC increases faster than the one of CNF. The conductivity range of CNC

Table 2. Testing parameters for measurement of tensile strength.

Test length at starting position	180.0 mm
Speed at starting position	400 mm/min
Pre-load	None
Test speed	20 mm/min
Turn-off threshold	50% F_{max}
Upper force limit	500 N
Power threshold for breaking test	0.5% F_{nom}

Table 3. pH-values of CNF and CNC suspensions from 0.5–3 wt%.

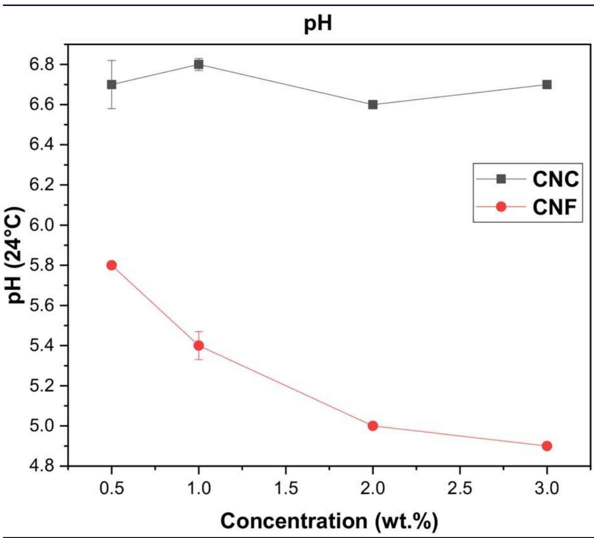


Table 4. Conductivity in µs/cm of CNF and CNC suspensions from 0.5–3 wt%.

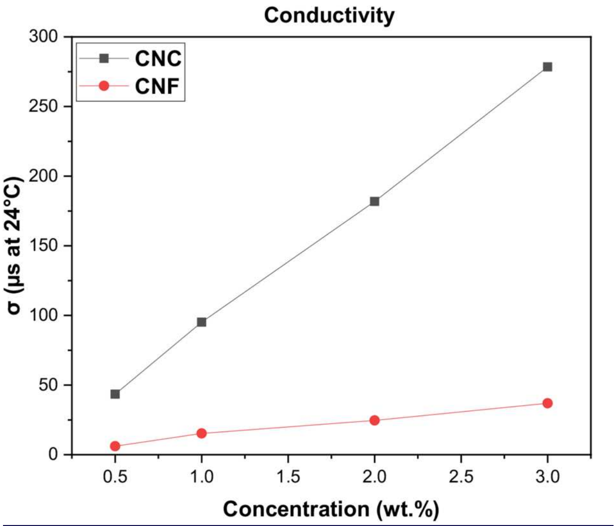
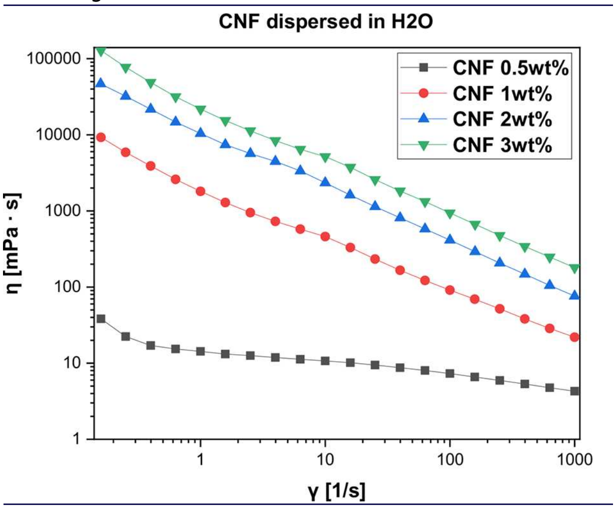


Table 5. Apparent viscosities of CNF 0.5–3 wt% in H_2O at increasing shear rates of 1–1000 [1/s].



is between 47 and 280 µS while the one of CNF is between 0.1 and 48 µS.

Rheology measurements show that CNF and CNC in water are both shear thinning. The suspensions apparent viscosity as the function of shear rate in the range of 1–1000 1/s is shown in Tables 5–8. As it can be seen, the apparent viscosity reduced as the shear rate increased, displaying a non-Newtonian shear thinning behaviour. As referred by Moberg et al. (2017: 24), this behaviour exhibited both by the unmodified CNC-materials and CNF samples is the expected behaviour for suspensions containing rod-like particles or fibrils since these tend to orient themselves and partly disentangle due to the flow leading to a lower viscosity as the shear rate increases. Moreover, at the same shear rate, the apparent viscosity of CNF, both in water and water with ethanol was the largest, while the apparent viscosity of the CNC was the

Table 6. Apparent viscosities of CNC 0.5–3 wt% in H_2O at increasing shear rates of 1–1000 [1/s].

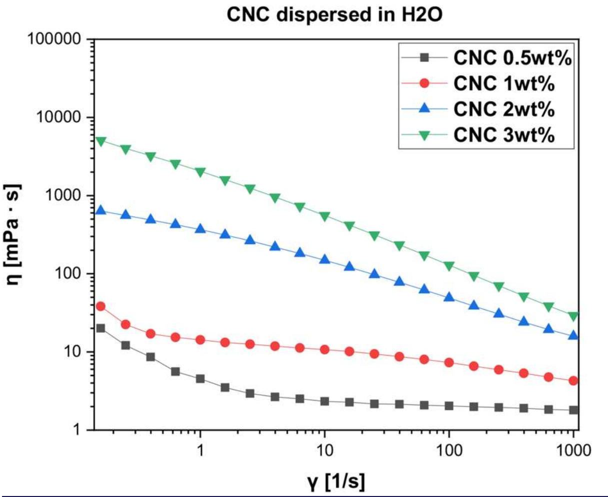


Table 7. Apparent viscosities of CNF 0.5–3 wt% in H_2O:EtOH at increasing shear rates of 1–1000 [1/s].

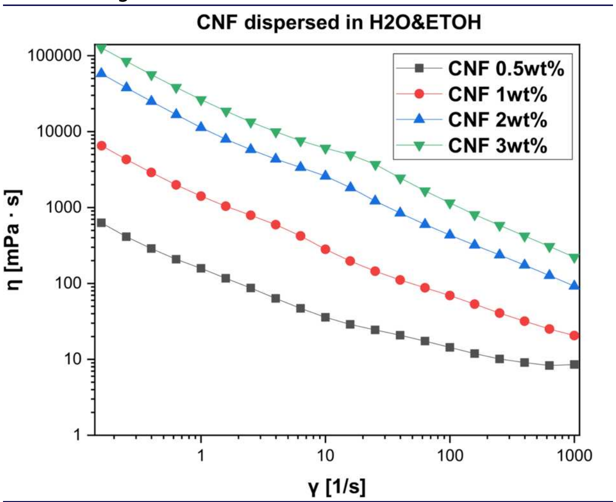
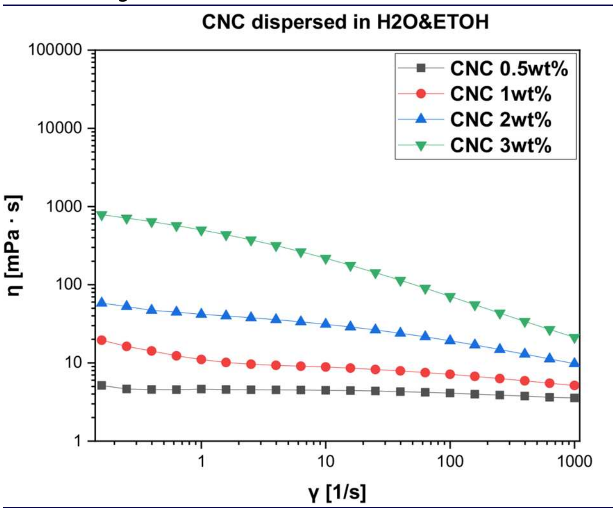


Table 8. Apparent viscosities of CNC 0.5–3 wt% in H_2O:EtOH at increasing shear rates of 1–1000 [1/s].



lowest. As expected, the increase in concentration resulted in a higher viscosity (Barnes et al., 1989).

Visual and haptic properties

The application of the CN in concentrations between 0.5 and 3 wt% in water has a neglectable influence on the optical appearance of the paper. Higher concentrations of 3 wt% CNF in water appear as matte, white hazes without gloss, while CNC in higher concentrations of 3 wt% in water tend to render the surface slightly shinier (Figure 5, right). Agglomerations of CNF in higher concentrations as 3 wt% are sometimes visible in printed areas as white lumps in black letters. Apart from that, the nano cellulosic suspensions do not veil the letters and are therefore superior to classical treatment options with Japanese paper, as Völkel et al. (2017: 8) have already stated and as can be seen in Figure 4.

Haptically the papers seem more stable, and the surface is to a minimal extent less smooth than before treatment for papers treated with 3 wt% CNF in water. Flexibility is not altered, while tension may occur with increasing amounts of CN, especially with CNC. Small tears which occur for example on the edges of the sheet cannot be mended by single application of nano cellulosic suspension.

In general, the visual and haptic properties (haze, gloss, smoothing, tension) of the treated samples correspond to the amount of material applied and are only minimally altered by the treatment.

Gravimetric analysis

Gravimetric analysis showed that the amount of material applied on Whatman® paper increases for CNF and CNC evenly from about 2 gm^2 at 0.5 wt% CNF to 18 gm^2 at 3 wt% CNF, respectively 4 gm^2 at 0.5 wt% CNC to 7 gm^2 at 3 wt% CNC. The increase of the amount of material applied is less homogeneous on newspaper, due to paper inhomogeneities, which lead to inhomogeneous penetration. The highest amount of material applied on newspaper lies at about 6 gm^2 for CNF and 10 gm^2 for CNC. The reduced water content results in a slightly reduced amount of material applied for both CNF and CNC on Whatman® paper. For the suspensions with reduced water content on newspaper, the weight after treatment corresponded in most cases the weight before treatment, indicating very poor CN penetration.

Fluorescence microscopy

The penetration behaviour of labelled CNC into a sheet of Whatman® No.1 was investigated by optical fluorescence microscopy using a UV filter on a cross-section of the treated paper (Table 9). As

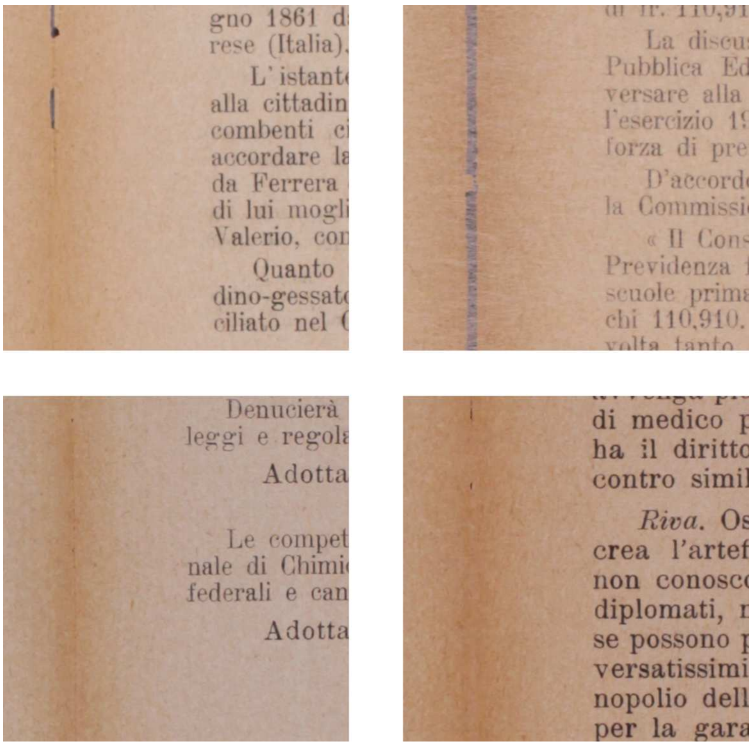


Figure 4. Historical paper from mechanical wood pulp untreated (top left), coated with Japanese paper 4 gm^2 (top right), coated with CNC 3 wt% (bottom left) and CNC 3 wt% + CNF 0.5 wt% (bottom right). The thin fibres of the Japanese paper are slightly veiling the writing in the text area. The coating with CNF and CNC has no negative effect on the appearance of the paper or the printed areas.

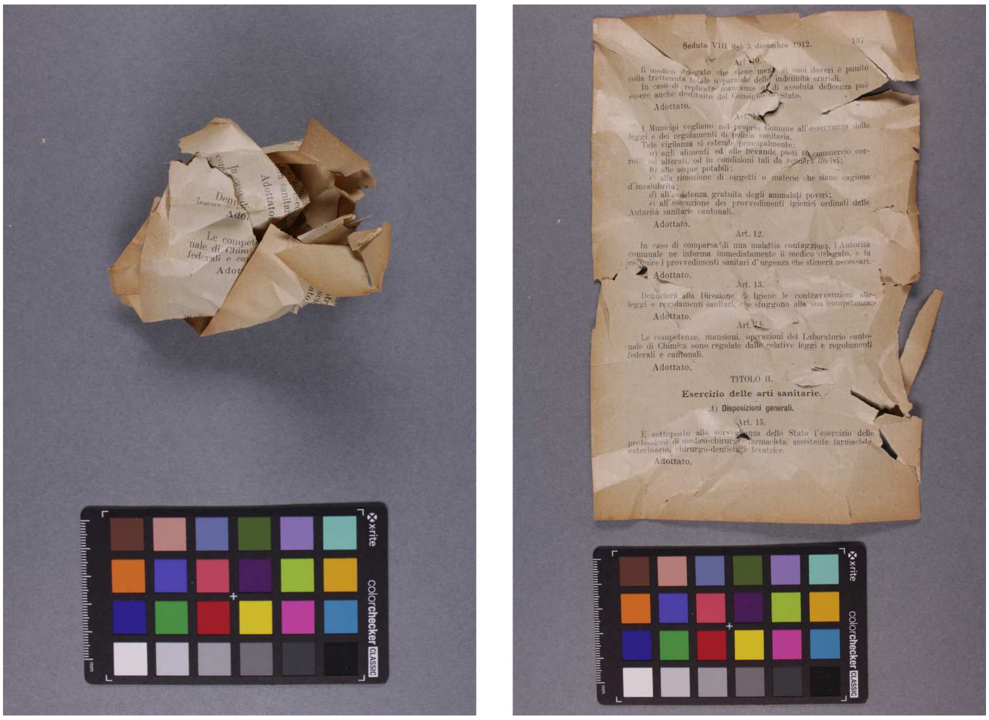


Figure 5. After treatment with CNC 3 wt%, the brittle and fragile historical paper still breaks at the creases after wrinkling but doesn't disintegrate into tiny pieces as the untreated paper. A strengthening of the paper structure has been achieved by the treatment with nanocellulose. At the same time, the coating with an amount of CNC as high as 3 wt% is visible just as a distinct gloss on the paper surface.

expected, the untreated Whatman® paper sample shows no fluorescence under UV light (a2) and serves as a reference. The intensity of the fluorescence of those samples that were immersed (b1 and b2) or coated (c1 and c2) with labelled CNC indicates a homogeneous penetration of the paper layer. This is visible in form of a light-yellow fluorescence distributed over the entire test area (b2 and c2). The emission is stronger for coated samples because more material is absorbed, whereas immersed samples show weaker fluorescence emission, because there is probably less suspension deposited. Looking at sample c2 also indicates that, when the paper is coated, the test has a penetration gradient showing a greater surface deposition of CNC (red fluorescence), and a lower penetration at the bottom of the cross section (bright yellow fluorescence). The fact that in this simple optical analysis the fluorescence spreads all over the paper cross section let's suppose that the CNC were able to successfully penetrate the paper and an increase in tensile strength is therefore to be expected in samples treated with CNCs. Fluorescence microscopy has not been investigated yet for samples of historical newspaper and with labelled CNF but will be carried out in the future.

pH

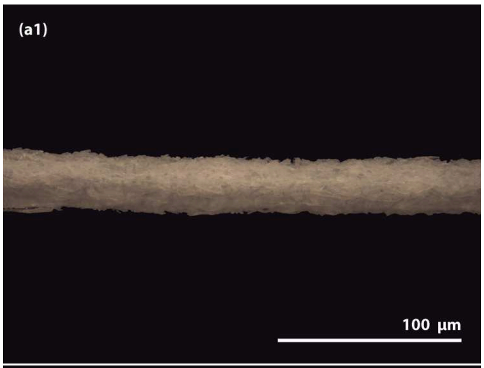
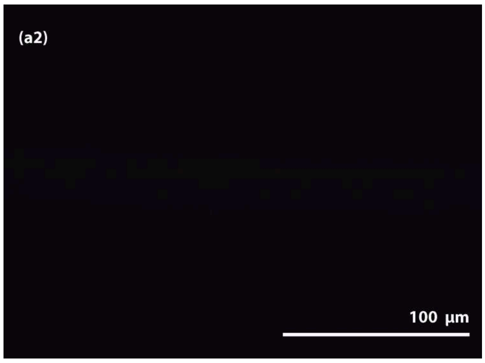
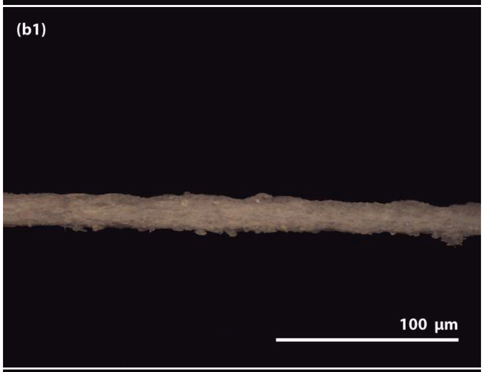
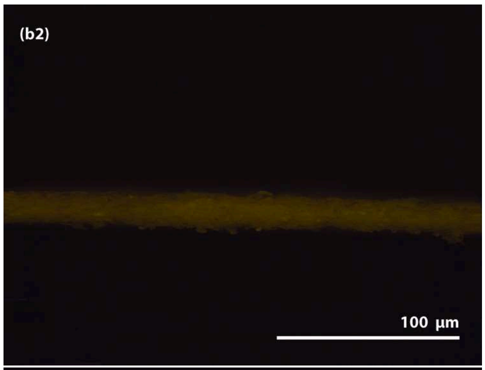
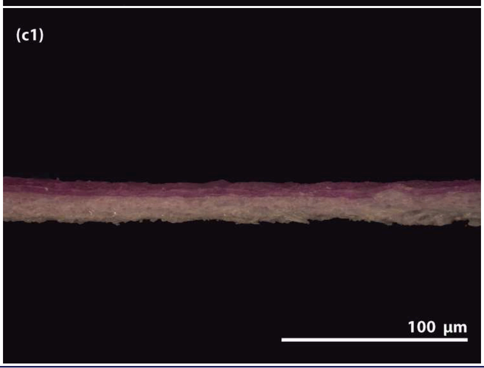
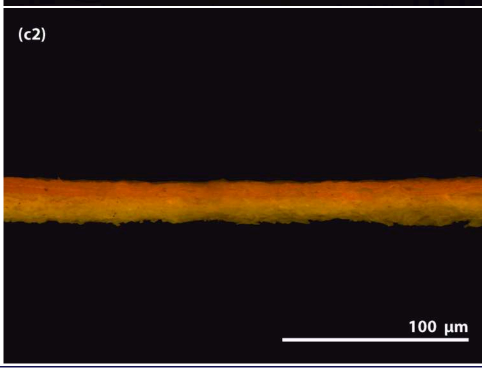
The pH according to ISO 6588-1: 2012 lies at 7.2 for the untreated Whatman® paper, at 7.1 for the paper treated with CNF and at 7.3 for the paper treated with CNC. The pH is not critically altered by the treatment with a single application of a 3 wt% solution of CNF or CNC. It is to expect that even for higher amounts of material applied there is probably no critical alteration of the pH value, and the treatment has no negative effect in this regard.

Paper stability

The mechanical properties of paper define its usability. Loss of strength is the natural consequence of the depolymerization of cellulose during ageing. Under mechanical stress due to wrinkling, an untreated historical newsprint breaks into small pieces (Figure 5, left). However, if this newspaper sheet is treated with a 3 wt% CNC aqueous suspension and thus reinforced, it still breaks at its folds (Figure 5, right), but the disintegration into innumerable small pieces does not occur as in Figure 1. This demonstration impressively confirms the measurement of the practical effect of the treatment.

The tensile strength of paper is an important measured variable for the description of paper condition. Figure 6 shows the mechanical properties of the Whatman® paper samples according to the measurement of tensile strength after folding. The treatment of Whatman® paper with CNF and CNC in water caused a continuous positive development of tensile strength. The increase of tensile strength is

Table 9. Fluorescence micrographs of cross sections of Whatman® no.1 untreated (a1 and a2) and treated with CNC 1 wt% marked with RBITC, respectively immersed (b1 and b2) and coated (c1 and c2). On the left column, dark field transmitted visible light images. On the right, dark field images excited with blue light.

	No filter	UV filter I3 Blue
Whatman® no. 1		
Whatman® no. 1 + CNC & RBITC (immersed)		
Whatman® no. 1 + CNC & RBITC (coated)		

higher for the suspensions with CNC, with the highest increase of almost 20 Nmm^2 respectively 52% compared to the reference material for the treatment with 3 wt% CNC. CNC with reduced water content also shows a continuous positive development, but with lower values than the suspensions without ethanol. The values for CNF with reduced water content also lie below the values for CNF without ethanol and do not show a continuous positive development. This is probably caused by the enhancement of aggregation with the addition of ethanol, which means a less uniform application. The treatment with the combination of 3 wt% CNC and 0.5 wt% CNF shows a minimal improvement in tensile strength compared to the treatment with 3 wt% CNC. This may be caused by the poor penetration of the combined suspension. But even the successive application does not improve the paper stability as anticipated.

The measurement of the tensile strength of the historical newspaper after treatment (Figure 7) does not show a continuous positive evolution but the values are scattered throughout, whether for the suspensions of CNF or CNC with or without reduced water content. One hypothesis for the inconsistent values may be the inhomogeneous properties of the paper, which also lead to much higher standard deviations. The other reason probably lies in the lower penetration of suspensions due to the hydrophilic character of the paper. The highest increase in tensile strength on historical newspaper was achieved by the application of 1 wt% CNF with 33% ethanol, which lead to an increase of about 2 Nmm^2 respectively 25% compared to the reference material. However, the pre-wetting with ethanol–water-mixture could significantly facilitate the penetration and lead to even higher values of paper strength. The pre-wetting and application of 3 wt% CNF with 33% ethanol led to an increase of about 4.5 Nmm^2 respectively more than 50% compared to the reference material. Please note that the y-axis of Figure 7, tensile strength for

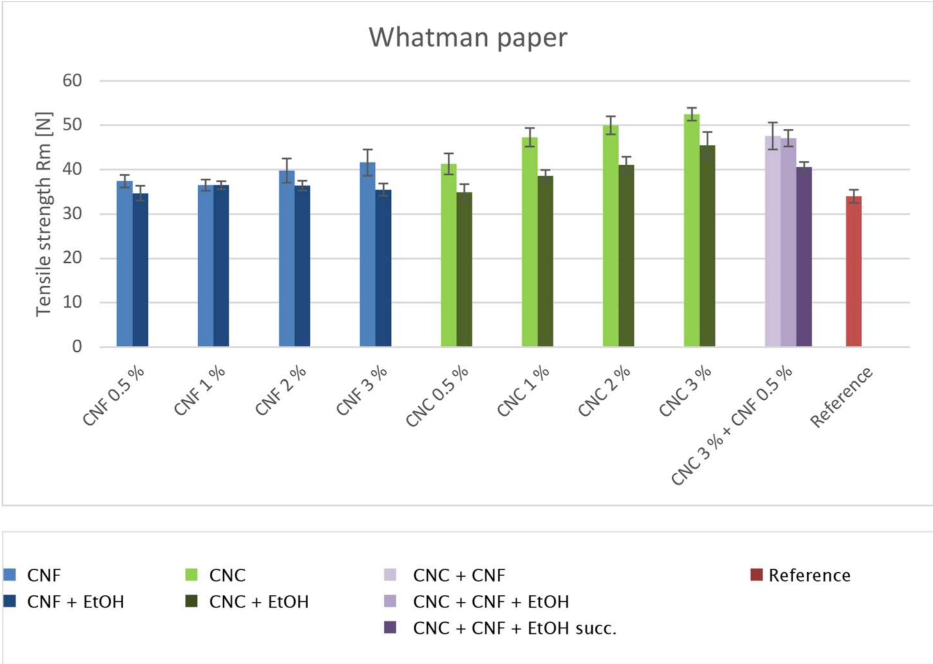


Figure 6. Measurement results of tensile strength for Whatman® paper treated with CNF and CNC.

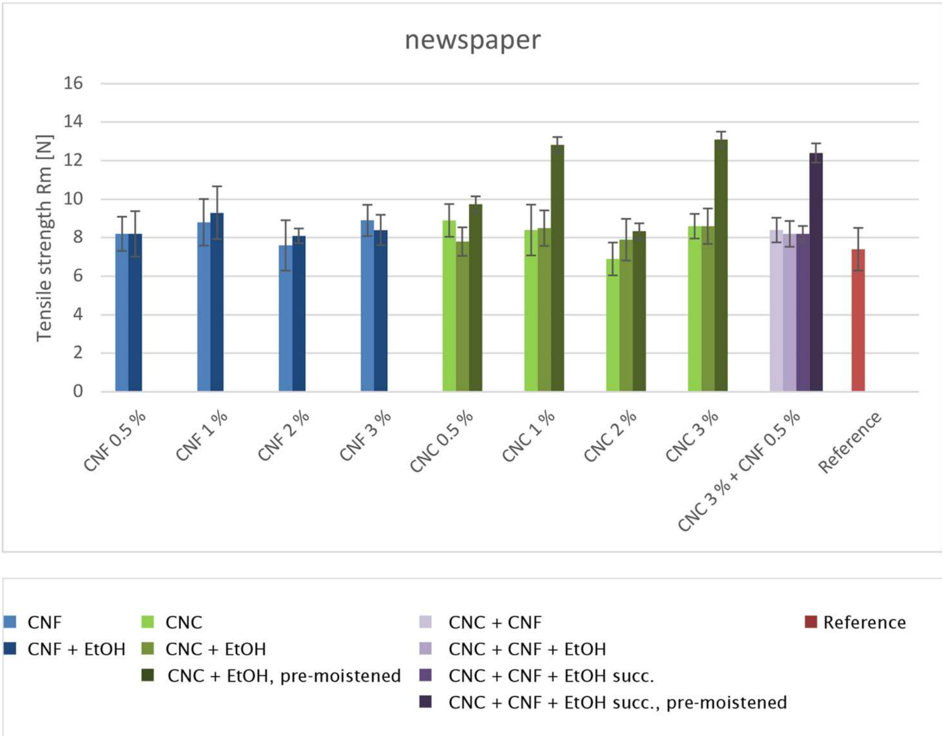


Figure 7. Measurement results of tensile strength for historical newspaper treated with CNF and CNC.

the historical newspaper, ranges from 0–16 N to display the results in a way that is better distinguishable, while the y-axis of Figure 6, tensile strength of Whatman® paper, ranges from 0–60 N.

The results for the measurement of tensile strength indicate the difficulty of applying a constant level of CN. However, it was possible to show that the treatment with nano cellulosic suspensions increases the tensile strength and therefore the mechanical stability of the paper in general. In the case of newsprint, prewetting improved the application and thus the increase in tensile strength resulting from the treatment.

Conclusions

In this study, a good treatability was achieved for both types of paper with CNF and CNC. An increase in viscosity, proportional to the amount of solid content, was observed for both CNC and CNF. The pH, optical and haptical properties, as well as the conductivity were not critically altered after treatment.

An increase of the mechanical properties has been reached for the samples treated with CNF as well as for those treated with CNC. In general, it can be assessed that the Whatman® paper, probably due to its high porosity, leads to greater values in terms of increased strength compared to the historical newspaper. The Whatman® samples coated with the 3 wt% CNC dispersed in water show the highest increase (approx. 52%) in tensile strength compared to the untreated reference and the suspensions dissolved in water reached better outcomes than those treated with EtOH. The great diffusion of the CNC into the Whatman® paper's matrix is also confirmed by the fluorescence microscopy which shows an overall distribution of the crystals. This means that the paper is not only stabilized on the surface, but also from within.

As to be expected, the historical newspaper, due to its surface inhomogeneity and more hydrophobic character, is more difficult to treat than the Whatman®. Reduction in the rate of penetration has led to a lesser effect of strengthening by the treatment with CNC and CNF in the historical newspaper. The pre-moistening of the paper with ethanol–water-mixture for lowering the surface tension could facilitate the application and the addition of an ethanol content of 33% in the suspension improved the treatment even more.

Again, better performances are achieved with CNC and the treatment with pre-moistening and CNC 3 wt% with an addition of 33% ethanol could increase the strength of the paper up to 50% compared to the untreated reference.

Interestingly, the use of CNF combined with CNC brought an increase of strength in the historical newspaper but seems to have just a minimal effect on the Whatman®. A successive application appears to have greater benefits than the combined suspension.

The goal of this research to improve paper stability through addition of unmodified nanocellulose has been successfully achieved, especially with the CNC. Further studies are necessary to investigate the possibility to achieve higher penetration of the nanocrystals, using less polar solvents than water aiming at reducing the risk of swelling of the fibres, and to study their long-term degradation and aging properties as well as different application methods. Currently, a master's thesis is investigating the use of CNC and CNF suspensions to strengthen historical paper containing mechanical wood pulp in a nineteenth century photo album.

Acknowledgements

We would like to thank the Laboratory for Cellulose and Wood Materials at Empa (Duebendorf, Switzerland) for the supply of nano cellulose, testing of samples and discussions. We are grateful to the conservation lab from the Swiss National Library (Bern, Switzerland) for providing the folding-device for the tensile strength measurements. Special thanks to Atelier Michael Rothe (Bern, Switzerland) for coating of samples with Japanese paper. We would also like to thank Brigitte Lienert-Pärli (formerly Hochschule der Künste Bern, Switzerland) for her support regarding pH-determination.

Disclosure statement

No potential conflict of interest was reported by the author(s).

Authors

Lucy Gmelch graduated in 2020 as a part-time student from the programme for Conservation-Restoration of graphics, written materials, and photography at Hochschule der Künste Bern (HKB), Switzerland (Master). Parallel to her studies, she was working several years at book and paper conservation workshops in Germany and Switzerland and is currently employed as a scientific associate at HKB. The initial research for this paper regarding the stabilization of degraded paper with nanocellulose material was the subject of a Minor Research during her Master studies.

Electra D'Emilio completed her MA Conservation-Restoration in Paintings and Sculpture at Hochschule der Künste Bern (HKB), Switzerland in 2018. During her studies she worked as a conservator in various studios and museums in Switzerland and Italy. She gained professional experience at Empa, where she was employed from 2019–2020 as research assistant in a project about wood glues for arts and cultural objects (*woodNANObonding*). Until 2023, Electra D'Emilio was working at the Institut für Materialität in Kunst und Kultur at HKB in different projects in the field of science applied to cultural heritage.

Thomas Geiger works at Empa, Swiss Federal Laboratories for Materials Testing and Research, Duebendorf, Switzerland, in the Cellulose and Wood Materials laboratory. He received his diploma in 1995 and completed his doctoral studies in 1998 at the Department of Chemistry, Pharmacy and Geosciences, Johannes Gutenberg University, Mainz, Germany. From 1998, he worked in the Corrosion and Surface Protection Laboratory at Empa. From 2003 to 2015, he led a group at Empa's Functional Polymers Laboratory as a research associate. His research interests are in the development, characterization and industrialization of multifunctional cellulose materials as well as biopolymer compounds.

Carmen Effner is a lecturer at Hochschule der Künste Bern (HKB), Switzerland, in the field of conservation and restoration of manuscripts as well as deputy director of the Institut für Materialität in Kunst und Kultur at HKB. She wrote her diploma thesis in 2008 at HKB on the topic 'Influence of mass deacidification (Papersave Swiss process) on paper damaged by ink corrosion'. From 2013–2015, Carmen Effner was a research assistant in the Innosuisse project 'Iron gall ink'. From 2021–2023, she was leading a research project funded by Innosuisse about the use of nanocellulose for the treatment of papers damaged by iron gall ink corrosion.

ORCID

Lucy Gmelch http://orcid.org/0000-0003-0076-2702
Electra Maria Letizia D'Emilio http://orcid.org/0000-0002-8619-6010
Thomas Geiger http://orcid.org/0000-0001-6555-8417
Carmen Effner http://orcid.org/0000-0002-1704-1250

References

Bansa, H. & Hofer, H.H. 1980. Die Beschreibung der Benutzbarkeitsqualität gealterter Papiere in Bibliotheken und Archiven. *Das Papier*, 34(8):348–355.

Barnes, H.A., Hutton, J.F. & Walters, K. 1989. An Introduction to Rheology. *Elsevier*, 3:1–199.

Camargos, C.H.M., Figueiredo, J., Pereira, J.C.D. & Fabiano, V. 2017. Cellulose Nanocrystal-Based Composite for Restoration of Lacunae on Damaged Documents and Artworks on Paper. *Journal of Cultural Heritage*, 23:170–175.

Dreyfuss-Deseigne, R. 2017. Nanocellulose Films in Art Conservation: A New and Promising Mending Material for Translucent Paper Objects. *Journal of Paper Conservation*, 18(1):18–29.

Dufresne, A. 2020. Preparation and Properties of Cellulose Nanomaterials. *Paper and Biomaterials*, 5(3):1–13.

EN 20187: 1993. 1993. *Paper, Board and Pulps – Standard Atmosphere for Conditioning and Testing and Procedure for Monitoring the Atmosphere and Conditioning of Samples*. Geneva: International Standard Organisation.

EN ISO 1924-2: 2008. 2008. *Paper, Board and Pulps – Determination of Tensile Properties – Part 2: Constant Rate of Elongation Method (20 mm/min)*. Geneva: International Standard Organization.

Groso, A., Petri-Fink, A., Rothen-Rutishauser, B., Hofmann, H. & Meyer, T. 2016. Engineered Nanomaterials: Toward Effective Safety Management in Research Laboratories. *Journal of Nanobiotechnology*, 14(21):1–17.

Harwood, A. 2011. Analysis of the Physical Characteristics of Transparent Cellulosic Nanofiber Paper. *WAAC Newsletter*, 33(2):12–15.

ISO 6588-1: 2012. 2012. *Paper, Board and Pulps – Determination of pH of Aqueous Extracts – Part 1: Cold Extraction*. Geneva: International Standard Organisation.

Moberg, T., Sahlin, K., Yao, K., Geng, S., Westman, G., Zhou, Q., Oksman, K. & Rigdahl, M. 2017. Rheological Properties of Nanocellulose Suspensions: Effects of Fibril/Particle Dimensions and Surface Characteristics. *Cellulose*, 24:2499–2510.

Nano-SDB-Leitfaden. 2016. *Sicherheitsdatenblatt (SDB): Leitfaden für synthetische Nanomaterialien*. Bern: Staatssekretariat für Wirtschaft (SECO).

Nielsen, L.J., Eyley, S., Thielemans, W. & Aylott, J.W. 2010. Dual Fluorescent Labelling of Cellulose Nanocrystals for pH Sensing. *Chemical Communications*, 46:8929–8931. https://doi.org/10.1039/c0cc03470c

O'Connor, B., Berry, R. & Goguen, R. 2014. Commercialization of Cellulose Nanocrystal (NCC™) Production: A Business Case Focusing on the Importance of Proactive EHS Management. In: M. S. Hull & D.M. Bowman, eds, *Nanotechnology Environmental Health and Safety*, 2nd ed. Oxford: William Andrew Publishing, pp. 225–246.

OECD. 1992. *Test No. 406: Skin Sensitisation*, OECD Guidelines for the Testing of Chemicals, Section 4. Paris: OECD Publishing. https://doi.org/10.1787/9789264070660-en.

OECD. 2010. *Test No. 429: Skin Sensitisation: Local Lymph Node Assay*, OECD Guidelines for the Testing of Chemicals, Section 4. Paris: OECD Publishing. https://doi.org/10.1787/9789264071100-en.

OECD. 2015. *Test No. 404: Acute Dermal Irritation/Corrosion*, OECD Guidelines for the Testing of Chemicals, Section 4. Paris: OECD Publishing. https://doi.org/10.1787/9789264242678-en.

Operamolla, A., Mazzuca, C., Capodieci, L., Di Benedetto, F., Severini, L., Titubante, M., Martinelli, A., Castelvetro, V. & Micheli, L. 2021. Toward a Reversible Consolidation of Paper Materials Using Cellulose Nanocrystals. *ACS Applied Materials & Interfaces*, 13:44972–44982. https://pubs.acs.org/doi/epdf/10.1021acsami.1c15330.

Perdoch, W., Cao, Z., Florczak, P., Markiewicz, R., Jarek, M., Olejnik, K. & Mazela, B. 2022. Influence of Nanocellulose Structure on Paper Reinforcement. *Molecules*, 27(4):1–16. https://www.mdpi.com/1420-3049/27/15/4696.

Revol, J.F., Bradford, H., Giasson, J., Marchessault, R.H. & Grey, D.G. 1992. Helicoidal Self-Ordering of Cellulose Microfibrils in Aqueous Suspension. *International Journal of Biological Macromolecules*, 14(3):170–172.

Santos, S.M., Carbajo, J.M., Gómez, N., Quintana, E., Ladero, M., Sánchez, A., Chinga-Carrasco, G. & Vilar, J.C. 2016a. A. Use of Bacterial Cellulose in Degraded Paper Restoration. Part I: Application on Model Papers. *Journal for Material Science*, 51:1541–1552.

Santos, S.M., Carbajo, J.M., Gómez, N., Quintana, E., Ladero, M., Sánchez, A., Chinga-Carrasco, G. & Vilar, J.C. 2016b. B. Use of Bacterial Cellulose in Degraded Paper Restoration. Part II: Application on Real Samples. *Journal for Material Science*, 51:1553–1561.

Shankaran, D.R. 2018. Chapter 14. – Cellulose Nanocrystals for Health Care Applications. In: Sneha Mohan Bhagyaraj, Oluwatobi Samuel Oluwafemi, Nandakumar Kalarikkal & Sabu Thomas eds, *Micro and Nano Technologies, Applications of Nanomaterials*. Woodhead Publishing, pp. 415–459, ISBN 9780081019719. https://doi.org/10.1016/B978-0-08-101971-9.00015-6.

Shatkin, J.A. & Kim, B. 2017. Environmental Health and Safety of Cellulose Nanomaterials and Composites. In: H. Kangarzadeh, I. Ahmad, S. Thomas & A. Dufresne, eds, *Handbook of Nanocellulose and Cellulose Nanocomposites, 2*. Weinheim: Wiley-VCH Verlag GmbH & Co. KGaA, pp. 683–729.

Soppa, K., Laaser, T. & Krekel, C. (2013) Lokalisierung von Konsolidierungsmitteln in Gemälden durch Fluoreszenzmarkierung. Teil I: Einführung in die Verfahrenstechnik und Anwendungsbeispiele bei aufstehender Malschicht auf textilem Bildträger. In: *ZKK Zeitschrift Für Kunsttechnologie und Konservierung* 195–217.

Völkel, L., Ahn, K., Hähner, U., Gindl-Altmutter, W. & Potthast, A. 2017. Nano Meets the Sheet: Adhesive-Free Application of Nanocellulosic Suspensions in Paper Conservation. *Heritage Science*, 5(23):1–17.

Völkel, L., Beaumont, M., Johansson, L.-S., Czibula, C., Rusakov, D., Mautner, A., Teichert, C., Kontturi, E., Rosenau, T. & Potthast, A. 2022. Assessing Fire-Damage in Historical Papers and Alleviating Damage with Soft Cellulose Nanofibers. *Small*, 18:1–14. https://onlinelibrary.wiley.com/doi/epdf/10.1002smll.202105420.

Zanetti, M. (2022) *New technologies for the conservation of written paper heritage damaged by fire*. PhD Thesis. Muséum national d'Histoire naturelle (MNHN) et Sorbonne Université and the University of Padua. https://theses.hal.science/tel-04181667v1.

List of suppliers

Alfa Aesar by Thermo Fisher Scientific, Thermo Fisher GmbH, Erlenbachweg 2, 76870 Kandel, Germany, Tel:

+49 721 84 00 72 80, www.alfa.com (sodium hydroxide, flake 98 %, A18395).

Anton Paar Switzerland AG, Pulverhausweg 13, 5033 Buchs AG, Switzerland, Tel: +41 62 745 16 80, www.anton-paar.com (rheometer Physica MCR 300 with DG26.7 double gap cylinder).

CelluForce Inc., 2000 McGill College Avenue, 6th floor, Montreal, Quebec, Canada H3A 3H3, Tel: +1 514 360 1023, www.celluforce.com (Cellulose nanocrystals NCC™).

Dr. Grogg Chemie AG, Gümligentalstrasse 83, 3066 Stettlen-Deisswil, Switzerland, Tel: +41 31 932 11 66, www.grogg-chemie.ch (ethanol 94 % denaturated with ketone G013.0250, potassium chloride Ph.Eur., USP, G286.9025).

GMW, Wilhelm LEO's Nachfolger GmbH, Kasseler Str. 84b, 34246 Vellmar, Germany, Tel: +49 561 982290, www.gmw-shop.de (Viledon thin, 30 gm^2).

Hach Lange GmbH, Rorschacherstrasse 30a, 9424 Rheineck, Switzerland, Tel: +41 848 55 66 99, www.ch.hach.com (HQd Portable Meter, pHC101 Electrode, CDC401 Electrode).

HUBERLAB. AG, Industriestrasse 123, 4147 Aesch, Switzerland, Tel: +41 61 717 99 77, www.huberlab.ch (Whatman® qualitative filter paper No. 1 in sheets).

Jenoptik AG, Carl-Zeiss-Strasse 1, 07743 Jena, Germany, Tel: +49 3641 65 0, www.jenoptic.de (digital SLR camera ProgRes® SpeedXT core 3 and corresponding PC software ProgRes® CapturePro 2.10).

Leica Camera AG, Am Leitz-Park 5, 35578 Wetzlar, Germany, Tel: +49 6441 2080 0, www.leica-camera.com (fluorescence microscope Leica Leitz DMRB, filter I3 Blue).

Masuko Sangyo Co., Ltd., 1-12-24 Honcho, Kawaguchi-city, Saitama, Japan 332-0012, Tel: 181 48 222 43 43, www.masuko.com (supermasscolloider MKZA10-20 J CE).

Mercer Stendal, Zellstoff Stendal GmbH, Goldbecker Str. 1, 39596 Arneburg, Germany, Tel: +49 39321 550, www.mercerint.com (elemental chlorine-free pulp ECF).

Merck KGaA, Frankfurter Strasse 250, 64293 Darmstadt, Germany, Tel: +49 61 517 20, www.merckgroup.com (Rhodamine B-isothiocyanat).

Metrohm Schweiz AG, Industriestrasse 13, 4800 Zofingen, Switzerland, Tel: + 41 62 745 28 00, www.metrohm.com (pH meter Metrohm 827 pH lab).

Swiss Federal Laboratories for Materials and Science and Technology, Department of Wood & Cellulose Materials, Ueberlandstrasse 129, 8600 Duebendorf, Switzerland, Tel: +41 58 765 4723, www.empa.ch (cellulose nanofibrils from eucalyptus).

ZwickRoell GmbH & Co. KG, August-Nagel-Str. 11, 89079 Ulm, Germany, +49 7305 10 -0, www.zwickroell.com (tensile testing machine zwickiLine Z 2.5).

Appendix

Recommended health and safety measures for working with nanocellulose materials.

The use of cellulose nanomaterials (CN) is considerably increasing in the paper industry for various purposes. Conservators are somewhat anxious about the use of engineered nanomaterials (ENM) since it is known that particles in nano size can easily be breathed through the nose and penetrate cells and organs. Therefore, specific information about the safe use of nanocellulose and its possible health risks are essential. ENMs as well as CNs often demonstrate properties that differ from the characteristics of the same material in the bulk form (Groso et al., 2016: 2). The occupational exposure limit (OEL) defines the upper limit of the acceptable concentration of a hazardous substance at the workplace. Currently, there are no specific regulatory OELs established for ENMs including CNs.

In Switzerland, there are no specific guidelines regarding the CN available yet. The Swiss safety data sheet (SDS) for synthetic nanomaterials offers information about the specific properties and possible risks of nanomaterials in general and is available in German, French, Italian and English (Nano-SDB-Leitfaden, 2016).

Shatkin and Kim (2017: 721) assess the currently existing knowledge about health and environmental impact of CN. They emphasize that the primary concern for a user of CN is the inhalation of pure, dried material during laboratory work and recommend controlling potential releases by making sure of engineering protocols (such as local exhaust ventilation or hoods and personal protective equipment PPE) during the handling of dry product composites until clear guidance on acceptable exposure concentrations is established. By using CN in a bound form in suspensions, the risk of inhalation is eliminated.

Standardized test guidelines for dermal testing (OECD TG 406, 404, 429) demonstrated that the CNC was non-sensitizing, noncorrosive, and not irritating to the skin (O'Connor et al., 2014: 233–236). No studies were found that involved eye contact exposure for either CNC or CNF (Shatkin & Kim, 2017: 702). If using suspensions of CN, gloves and safety glasses are recommended to decrease the potential for dermal or eye exposure. CN are presumed to be a low hazard to the environment (Shatkin & Kim, 2017: 724), so the disposal of small amounts of nano cellulosic suspensions via regular sewer is possible.