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# The consolidation of depolymerized cellulosic textiles: observations and open questions on the use of cellulose nanocrystals as a consolidant

# A consolidação de têxteis celulósicos despolimerizados: observações e questões em aberto sobre o uso de nanocristais de celulose como consolidante

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**Abstract**

As with any other material, canvases are susceptible to degradation, which leads to a loss of the textiles' ability to support the paint layers. Lining has historically been the prevalent method for addressing the issue. However, the risks associated with this approach have been widely documented, prompting a shift towards alternative solutions. The use of cellulose nanocrystals (CNC) for consolidation treatment represents a bio-based alternative to conventional conservation products, with advantages in terms of compatibility and sustainability. Building upon prior studies, ongoing doctoral research aims to enhance the understanding of key issues pertaining to CNC, which have been insufficiently explored in previous studies. These include aspects such as CNC penetration into the substrate, its adhesion to the canvas, and methods for reducing the quantity of water required for its application. The primary objective of the current study is therefore to clarify the possibilities and limitations of a promising eco-friendly material.

**KEYWORDS**
Nanocrystalline cellulose (CNC)
Nanocellulose
Nanomaterials
Green conservation
Canvas consolidation
Sustainability

**Resumo**

Tal como qualquer outro material, as telas são suscetíveis à degradação, levando à perda da capacidade dos têxteis de suportar as camadas de tinta. Historicamente, o revestimento tem sido o método predominante para resolver o problema. Os riscos associados a esta abordagem têm sido amplamente documentados, encaminhando para soluções alternativas. A utilização de nanocristais de celulose (CNC) para o tratamento de consolidação representa uma alternativa biológica aos produtos de conservação convencionais, com vantagens na compatibilidade e sustentabilidade. Com base em estudos anteriores, a investigação de doutoramento em curso visa aprofundar a compreensão de questões-chave relacionadas com os CNC, que não foram suficientemente exploradas em estudos anteriores. Estas incluem aspetos como a penetração dos CNC no substrato, a sua adesão à tela e métodos para reduzir a quantidade de água necessária para a sua aplicação. O objetivo principal deste estudo é evidenciar as potencialidades e limitações de um material ecológico promissor.

**PALAVRAS-CHAVE**
Celulose nanocristalina (CNC)
Nanocelulose
Nanomateriais
Conservação ecológica
Consolidação de telas
Sustentabilidade

## Introduction

This paper presents the premises and main objectives of a doctoral research project that is currently conducted as part of the national PhD program in Heritage Science (Cycle XXXIX), coordinated by La Sapienza University of Rome. This research belongs to Curriculum 1 (CV1), coordinated by the University of Florence. CV1 focuses on "Advanced materials and methodologies for safeguarding cultural heritage: ecological and digital transition for mitigating anthropogenic and natural risks". The project here briefly described is being carried out at the laboratories of the Central Institute for Restoration (ICR) of Rome and will address the potential of cellulose nanocrystals (CNC) for the consolidation of depolymerized cellulosic canvases. The main objective of the research is to better define whether CNC can represent an environmentally friendly alternative to traditional consolidation products.

## Consolidation of depolymerized canvases

Paintings on canvas are physical systems characterised by complex stratigraphies, and each of their constituent parts is subject to natural ageing processes and alterations of various kinds. These processes are triggered or exacerbated by the environmental conditions as well as other factors, which often act simultaneously and synergistically. The outcome is a series of modifications generally recognised as forms of degradation. Cellulose fabrics, commonly used as canvas supports for paintings, are no exception and undergo progressive deterioration, compromising their role as structural supports for pictorial layers.

The mechanical properties of cellulose essentially depend on the integrity of its polymer chains; therefore, their shortening produces a weakening of fibres, yarns, and ultimately the textile [1, p. 54]. The degree of polymerisation (DP), which quantifies the number of monomeric units in a polymer, is therefore an indicator of the fibres' tenacity, even though mechanical resistance is also influenced by polymer chain morphology and supramolecular structure. Polymer chains cleavage can occur as a result of different reactions, but among all of them, acid hydrolysis is generally considered to be the most relevant. Chemical degradation predominantly affects the amorphous zones of cellulose, which are more reactive and accessible compared to the crystalline regions. Hence, as these flexible amorphous zones diminish, the material's mechanical properties undergo drastic modifications, leading to severely reduced tensile strength and increased fragility.

This process has repercussions on the conservation of the ground and paint layers that the canvas is supposed to support, which are subject to increasing mechanical stress, resulting in the formation of *craquelure*, loss of adhesion, and eventually paint loss. A possible remedy to this mechanism involves the use of a consolidating product, whose ultimate aim is to restore the canvas's load-bearing capacity without relying on an auxiliary support. Consolidants act by linking and binding the damaged fibrous material; however, they cannot restore the integrity of the interrupted polymer chains. Currently, no material can re-establish the broken chemical bonds of cellulose, thereby increasing its DP, or reverse the degradation processes it has undergone. Instead, it is possible to re-establish cohesion of the material at a higher structural level, involving yarns and fibres rather than the polymer chains.

In order for depolymerized canvases to regain effectiveness as supports for paintings, it is an absolute prerogative for the applied product to restore adequate tensile strength and sufficient rigidity. Anyway, consolidation treatment is only effective when the DP is not excessively reduced. In the event that the physical characteristics of the canvas are compromised to an excessive degree, a more substantial structural intervention will probably be necessary. Although lining is connected to a series of well-known risks, sometimes it still represents the only option to provide adequate support to extremely deteriorated paintings on canvas.

Consolidation is correctly defined as the re-establishment of a degree of cohesion deemed sufficient in a material that, due to degradation processes, has lost its original aggregation characteristics [2, p. 217]. The attractive forces exerted between the microstructural elements of a material may weaken, leading to the formation of discontinuities in the structure of varying degrees, from the sub-microscopic to the macroscopic level. Consolidation generally occurs by impregnating the compromised material with a product applied in a fluid state, generally solubilised or dispersed. A specific characteristic of consolidant products is that they should also homogeneously affect the internal portion of the material to which they are applied. So, they ideally penetrate the internal structure of the material thanks to their low viscosity, ensuring uniform application and avoiding material accumulations. It should be noted that the concept of cohesion is commonly associated with various material properties, including tenacity, compactness, and elasticity, sometimes leading to ambiguity about the specific improvements consolidants should provide. So, to determine the ideal properties of a consolidant, several factors should be considered and require the understanding of the substrate's original characteristics, the degradation mechanisms affecting it, and its interactions with other components of the artwork. As for cellulosic fabrics that constitute the support of paintings, their relationship with the paint layers is a factor of primary importance to be considered [3, p. 19]. The canvas' tensile strength is essential, as it must withstand constant mechanical stress to remain tensioned on its stretcher. Also, as it is well known, maintaining appropriate tension levels is crucial for the preservation of paintings on canvas [4].

Given the intrinsically invasive and often irreversible nature of consolidation, due to the impregnation of the material with a product that is difficult to remove completely, two primary approaches are adopted. The first prioritises compatibility with the original material to minimise the risk of undesired or unforeseeable changes, while the second prioritises stability and durability, putting in the background material affinity.

Historically, several products were used as consolidants, usually polymeric materials in the form of solutions, dispersions, or emulsions. Animal glues like hide glue were common consolidants due to their affinity with the materials in many artworks, especially the size of many canvas paintings. More recently, the use of synthetic resins has been favoured because of their good performance, stability, and durability. Among these kinds of products, special mention must be made of Paraloid B72, which has often been applied on the back of canvases not only because of the need to re-establish adequate physical-mechanical properties, but also to reduce the cellulosic material's susceptibility to environmental fluctuations. Another commonly used acrylic resin is Plexisol P550, a homopolymer based on n-butyl methacrylate in solution, with excellent adhesive and optical properties. Also, a product specifically designed for structural preservation of textile substrates was the Akeogard AT35 (formerly Purbinder pa531), an aliphatic polyurethane resin in water dispersion, valued for its high tensile elongation, which has been widely used in the recent past on fibrous materials [5].

It is worth mentioning also that the application of adhesives on the back of paintings on canvas is sometimes dictated by different intentions rather than to consolidate the fabric: i.e., to re-establish the adhesion of the paint layers, exploiting the canvas's permeability. Even in this circumstance, although not the primary objective of the intervention, the support remains heavily involved because of the impregnation related to the use of the adhesive. Similarly, traditional lining methods, such as some glue-paste or wax-resin techniques, can result in impregnation of all layers of the painting.

On the basis of these considerations, it's possible to identify several key factors to evaluate the suitability of a consolidant for cellulosic fabrics. Ideal consolidants should:

- Restore adequate tensile strength, while not affecting too much flexibility, and elasticity;
- Be chemically compatible with the substrate and its components, including those introduced during past restorations. They should also have good behavioural compatibility, i.e., thermal expansion coefficient and hygroscopicity;
- Be chemically stable, maintaining appropriate solubility and mechanical properties even after prolonged ageing;

- Exhibit low viscosity and surface tension for homogeneous penetration and to avoid localised accumulations that would become the cause of potentially damaging internal tensions [6];
- Have an appropriate setting time to allow thorough application, but not too prolonged to avoid possible swelling or adverse reactions in the pictorial layers;
- Have a low aesthetic impact, avoiding perceptible optical changes of the substrate;
- Be removable or retractable to permit future interventions, also with different materials;
- Allow versatile application methods;
- Be soluble/dispersible in low-toxicity or non-toxic solvents and be environmentally friendly.

This study investigates the potential of crystalline nanocellulose as a consolidating agent for degraded cellulosic canvases. Recent research [7-22] has highlighted its potential, but further exploration is nonetheless needed to fully understand its applications and benefits in the field of conservation.

## Nanocellulose in cultural heritage conservation

Recently, various nanostructured materials have been introduced into the field of cultural heritage conservation due to their remarkable results in a wide range of applications, even when used at low concentrations. The study of biopolymers such as nanocellulose aligns with the growing trend of ecological transition in conservation, promoting the development of environmentally friendly restoration methodologies and materials. This research also fits into the broader context of studies investigating nanostructured materials in cultural heritage applications.

Nanocellulose is a nanomaterial [23] obtained by means of specific processes from raw materials consisting of cellulose, the most abundant natural biopolymer on the planet. It is therefore sourced from renewable materials [24]. Nanocellulose combines the inherent properties of the starting polymer – cellulose – with those arising from the nanoscale size of its particles. Key features of the material include outstanding mechanical properties, high surface area, biocompatibility, low density, suspension stability, and the possibility of functionalisation, along with non-toxicity. Nanocellulose exhibits a high surface area-to-volume ratio, which enhances its surface reactivity and influences properties such as dispersibility in solvents. This is a common feature of nanostructured materials. Since the surface molecules are not surrounded by as many other molecules as possible, they have fewer interactions that make them more reactive, influencing many properties of the material. This condition determines that the physico-chemical characteristics are more influenced by the surface molecules than by the internal ones, as they are present in proportionally larger quantities than in bulk form.

Although at present there is still no agreed-upon terminology, three types of nanocellulose are generally distinguished according to their characteristics and the production process by which they are obtained: these are cellulose nanocrystals (CNC), nano-fibrillated cellulose (NFC), and bacterial nanocellulose (BNC). Bacterial nanocellulose differs from the other two types because it's produced using a bottom-up process, as it is synthesised from simpler molecules by certain species of bacteria (*Acetobacter*, *Rhizobium*, *Agrobacterium*, and *Sarcina*), whereas CNC and NFC are obtained using top-down methods, breaking down complex structures into nanoscale components [25]. The source materials for CNC and NFC are essentially plants, wood, algae, straw, and other cellulose materials, which are subjected to chemical or mechanical processes that separate the nanometric components of the starting biopolymer from the other substances that may be present, such as encrustations in stem plants. The ratio between the length and diameter of the particles, as well as their morphology and degree of crystallinity, greatly influences the mechanical properties of the material. These parameters are, in turn, dependent on the source from which the material was obtained and the conditions under which the production process took place (Table 1).

**Table 1.** Main characteristics of the three types of nanocellulose (cellulose nanocrystals – CNC, nano-fibrillated cellulose – NFC, and bacterial nanocellulose – BNC).

| | CNC | NFC | BNC |
|---|---|---|---|
| Sources | Cotton, linen, hemp, straw, algae, wood, etc. | Cotton, linen, hemp, processing waste, etc. | Glucose |
| Main productive process | Acid hydrolysis | Mechanical process of defibrillation | Biochemical synthesis |
| Particles morphology | Thin, linear, unbent needles and rods | Long particles made of alternating amorphous and crystalline zones | Tridimensional porous network made of nanofibers |
| Average particle diameter | 5-70 nm | 4-20 nm | 20-100 nm |
| Average particle length | 100 nm – a few µm | A few µm | 100 µm |

CNC particles have a needle-like morphology with a significantly greater length than diameter. The material has a high crystallinity index of around 89 %, which is associated with a high modulus of elasticity, making it exceptionally resistant to deformation. CNC suspensions possess low density and are colloidally stable, so they do not require the use of surfactants.

**Advantages of CNC**

As aforementioned, by virtue of its remarkable characteristics, CNC has aroused the interest of conservators, who have been evaluating its possible uses in conservation for some years now. The main reasons for interest in nanocellulose as a restoration material lie in some of its characteristics, namely:

- High compatibility with cellulosic materials;
- Exceptional mechanical resistance;
- Transparency in films and suspensions;
- Barrier effect against gases and vapours;
- Possibility of functionalisation;
- Low specific weight (1.5 g/cm$^3$);
- Eco-sustainability;
- Cost-effectiveness.

For these reasons, it is believed that nanocellulose may represent a promising alternative to traditional polymers used for textile consolidation, reducing environmental and health risks while offering potential advantages in terms of compatibility, performance, and sustainability of the intervention. Indeed, the use of CNC could help to obtain the desired result by minimising further alterations to the values or characteristics of the work that cannot be foreseen or are undesirable [26].

**Limitations and challenges**

The notion of compatibility in art conservation has evolved over time. It has rightly been argued that the concept of compatibility has often been called upon to support the uncritical use of natural materials or to discredit the use of synthetic ones. This is the result of a simplistic and now largely outdated interpretation of the concept. While natural materials are often presumed to be more compatible with historical objects, this assumption is not universally valid. The complexity of cultural heritage objects, compounded by past interventions, requires a nuanced approach. On the other hand, it is also legitimate to argue that the similarity between the components of a restoration product and those constituting the work determines an objective greater probability that undesirable variations are not imparted to it, “distorting” it. Therefore, CNC must undergo thorough testing to evaluate its mechanical, chemical, and long-term stability characteristics. The potential limitations associated with the utilisation of CNC for the consolidation of canvases pertain to the possibility of its dispersion in water or hydroalcoholic mixtures. It is important to note that potential limitations associated with the utilisation of CNC can be attributed to two primary factors. Firstly, there is a propensity for the formation of a surface film, and secondly, there is its inherent hygroscopicity. Concerning the first aspect, in contrast to the anticipated behaviour of a nanometric material, numerous studies have observed the propensity of the CNC to accumulate on the fabric's surface. Despite the absence of a comprehensive investigation into the underlying causes of this phenomenon, the extent of material penetration and dissemination remains to be elucidated. A lack of adequate penetration could result in certain limitations on its use as a consolidant. However, it should be noted that this approach also offers theoretical advantages in terms of removability. Furthermore, it must be considered that CNC is the least hygroscopic kind of nanocellulose, due to its higher degree of crystallinity compared to CNF and BNC. Nevertheless, it exhibits a residual affinity for water, which clearly represents a potential limit, as it often represents an issue of the water sensitivity of many artworks.

**Studies on nanocellulose in conservation**

In recent years, studies have explored nanocellulose's potential for cultural heritage conservation, especially demonstrating its effectiveness in consolidating degraded wood and paper [27-28] and creating ultra-thin transparent films for repairing fragmented or torn paper artifacts [29-30]. A further possibility considered, already widely experimented in the industrial sphere, concerns the possibility of adding nanocellulose as a filler to different types of polymeric materials to enhance their mechanical properties and alter various properties, including gas permeability.

***Textile conservation potential***

More recent research has carefully investigated nanocellulose's use on textile fibres. Especially, the potential of CNC and NFC has been evaluated [16, 18-19]. It has been noted that for CNC, there is less difference in the Young's modulus detected at different RH levels than for CNF, even less than for the untreated sample (which is surprising as the material possesses hygroscopic sulphate groups). This is explained by the greater compactness of the film produced by CNC; however, it may also be attributed to the barrier effect operated by the material against water vapour. It has also been reported that CNC shows a large difference in E values as the RH varies, which is also greater than the difference measured for animal glue. This is probably because the glue needs more time to swell than that used for the test. In any case, it must be considered that at RH values greater than 80 % the glue gels, losing its consolidating abilities, while CNF does not. Furthermore, animal glue below 40 % RH can undergo contractions potentially harmful to the painting. The studies conclude by stating that, in the first instance, CNC seems to perform better than CNF in terms of mechanical reinforcement obtained and long-term stability. Further studies examined composite systems in which the nanometric material was added to polymeric matrices of different types [15, 31]. In other cases, versions of nanocellulose functionalised in different ways were tested [15, 19, 32]. In all these cases, tests were mostly conducted on cotton models, more rarely on linen, and only in a few cases, as far as is known, were the materials eventually applied to real paintings [10, 14-15].

All the studies known at present have confirmed the effectiveness of nanocellulose in providing a considerable increase in the mechanical characteristics of fibres, especially in the elongation region of interest, below 2 %, where structural reinforcement is most critical [21]. Above this threshold, the induced deformation is known to be irreversible, and the possibility of deterioration of the paint layers is high. The overall effect of nanocellulose application can be described as a stiffening of the fibrous structure of the canvas, which is more resistant but less deformable. In prior studies [14], CNC provided mechanical reinforcement comparable to synthetic resins like Plexisol P550 and Beva 371 O.F. (applied at much higher concentrations, i.e., 15 %). So, the resulting textile is stiffer and less deformable, improving its breaking load without substantially altering its thermal-hygrometric reactivity. This is a noteworthy difference from synthetic polymers used for the same purpose. The various studies confirm that nanometric cellulose does not alter the appearance of the consolidated material. It was also found that the nanocellulose, regardless of type and contrary to what would be suggested by its nanometric size, does not seem to penetrate the yarn structure; instead, it mostly settles on the surface to form a compact film, even though in a case good penetration was observed, probably because of the lack of size [10]. It has also been suggested that some types of nanocellulose (CNC and CCNF, or carboxymethylated nanofibrillated cellulose) may develop acidic characters as they age [21], but this has been ruled out by recent research [20].

## Research questions

Building on existing literature and prior studies, the research project explores underinvestigated aspects of crystalline nanocellulose (CNC) as a consolidant.

CNC was preferred to other types of nanocellulose because of its high degree of crystallinity: this leads, on the one hand, to better mechanical characteristics, while the lower presence of amorphous portions results in a lower hygroscopicity and vulnerability to degradation. Ethical considerations were also raised, depending on the tendency of nanocellulose to produce a surface coating rather than spread within the microstructure of the yarn, enabling greater theoretical reversibility compared to traditional consolidants. This could be of utmost relevance since it could help in pursuing the ideal of reversibility that guides any restoration intervention. Furthermore, CNC has the considerable advantage, compared to synthetic resins, of not producing substantial alterations in the hygroscopicity of textiles. Its eco-sustainability and reduced impact on operator safety further underscore its potential as a more sustainable alternative in restoration.

The focus is therefore on clarifying its potential and limitations while addressing critical factors that influence its suitability and effectiveness. Key objectives include the following aspects.

**CNC penetration**

While previous studies have noted surface film formation via scanning electron microscopy (SEM) [8, 16, 18-19, 21-22], the distribution of CNC within the substrate thickness has not been comprehensively analysed, although it is closely related to the mechanical performance of the product, as well as to the possibility of its removal. Some authors have proposed hypotheses on the cause behind this unexpected behaviour of nanocellulose, without, however, going into more detail. Based on the above, the main objective of the study will be to develop suitable methodologies to observe the material's distribution, leveraging advanced microscopy techniques and marker-based analysis, with a focus on correlating distribution patterns to mechanical performance and removability. Several possibilities are being considered in this respect, and tests are ongoing.

**Substrate interactions and surface contaminants**

The ability of CNC to establish interactions with the substrate and any limits determined by the presence of extraneous materials on the surface have not been studied thoroughly yet. Interactions established between nanocellulose and cellulosic canvases are substantially limited to the intermolecular bonds that are established between the two materials due to their chemical affinity, i.e., hydrogen bonds. Therefore, the adhesion between nanocellulose and canvases is mainly dependent on these interactions, so arises the need to verify the material's ability to adhere and consolidate effectively, even canvases that have already undergone restoration, where heterogeneous materials may be present, such as adhesive residues from lining. Therefore, this study will define the limits of CNC applicability.

In order to evaluate this aspect, a methodology drawn from recent scientific literature [8, 18-19] that exploits the capabilities of the atomic force microscope (AFM), appropriately adapted. The data obtained will then be correlated with the mechanical performance and surface morphology data, supported by SEM observations and surface roughness measurements. Also, the addition of a different material to the CNC as an adhesion promoter will be tested. The adhesive chosen for the production of the nanocomposite is a cellulose ether – hydroxypropyl cellulose (Klucel E) – due to its particularly low viscosity and affinity with nanocellulose [33].

**Minimizing water usage in CNC applications**

The recognized limitations and potential areas for improvement in the use of nanocellulose are largely associated with its restricted dispersibility in water or hydroalcoholic mixtures. This poses a significant challenge, as many artworks exhibit pronounced hygroscopic properties, with one or more of their components often being sensitive to water. Addressing this issue necessitates further investigation, beginning with an evaluation of alternative application methods, such as spraying of the material. Comparative studies will also be conducted to assess the differences in penetration and mechanical performance between materials applied by brush and those applied through nebulization. The use of emulsifying agents to enable the dispersion of nanocellulose in organic solvents could be another possible solution. However, this approach introduces additional complexities, particularly due to the potential biodegradability of many surfactants commonly employed as emulsifiers. An alternative strategy lies in the chemical functionalization of nanocellulose, leveraging its high reactivity owing to the presence of numerous hydroxyl groups. Among the possible reactions, silanization is particularly promising as it allows the dispersion of nanocellulose in non-polar solvents, therefore mitigating risks associated with water exposure.

Since the adhesion of nanocellulose to substrates primarily depends on interactions involving its hydroxyl groups, as previously stated, it is reasonable to hypothesize that silanization could compromise some of these interactions. However, the first studies suggest otherwise [15]; no significant differences have been observed between systems dispersed in polar and non-polar solvents regarding structural reinforcement. Instead, variations have been noted in optical properties and the application process, with non-polar solvent systems demonstrating higher volatility and reduced ease of use. The potential impact of reduced hydroxyl group availability on the hygroscopic behaviour of the material remains mostly underexplored.

These findings suggest that the performance of functionalized nanocellulose is comparable to that of unmodified nanocellulose in terms of interaction with substrates, even after aging. Thus, functionalization emerges as a promising line of research, especially because it could make applications to water-sensitive materials safer, despite the requirement for toxic solvent-based systems. Hence, future research will focus on direct comparisons between functionalized and unmodified nanocellulose to further evaluate their respective merits in conservation applications.

## Methodological approach in the evaluation of CNC as a consolidant

A prerequisite for all tests aimed at evaluating the selected parameters is the preparation of appropriate mock-ups. Specifically, the study uses oil paintings on canvas as reference models. The methodology employed in the creation of the samples necessary for the execution of tests and analyses was developed according to the criteria of maximum likelihood possible compared with antique paintings, homogeneity, as well as standardization and reproducibility of the procedure. The technical and material accuracy of the samples was assured by replicating the recipe of a reliable artistic source [34, fl. 114], suitably adapted, and regarded as representative of a broad range of paintings. The practical implementation has also been carried out with every possible precaution to ensure the samples are as homogeneous and comparable as possible. Furthermore, meticulous care was taken to create different groups of samples, with samples belonging to various areas of the starting canvas, to avoid errors due to possible localised defects.

**Mock-ups production**

Linen fabric was chosen as the substrate, given its historical prevalence as a fibre used for the production of painting canvases. The canvas underwent a preliminary depolymerization process through immersion in a 1 N nitric acid bath for ten days, in order to obtain physical properties comparable with those of ancient paintings (Figure 1). The method was adapted from a process known in the literature [35] and already successfully employed [14].

To assess the impact of consolidants on the various layers of a canvas painting, two distinct types of mock-ups were produced:

1. Mock-ups consisting of depolymerized canvas, without additional layers.
2. Mock-ups replicating the stratigraphy of an ancient oil painting, including size, ground layer, and paint layer.

This approach enables the evaluation of the consolidants' effects on both bare canvas and stratified systems, acknowledging previous studies [14] that demonstrated variable behaviour depending on the presence of paint layers. Specifically, nanocellulose has been observed to increase elongation at break in bare canvas samples, a behaviour not replicated in those with additional preparatory or paint layers. The stratigraphic samples were prepared following a procedure described in a seventeenth-century source [34, fl. 114] (Figure 2). Most of the samples were produced according to ISO 13934-1 (2013) guidelines, which regulate tensile testing parameters for textile samples.


**Figure 1.** For the depolymerisation of the textile, the linen canvas is put into an acid-resistant box, and glass plates are put on it to reduce its volume. Then, the acid is poured into the box until the canvas is fully submerged. Whereas for this procedure the reference article used a mixture of sulphuric acid and hydrogen peroxide, nitric acid was chosen for this case.

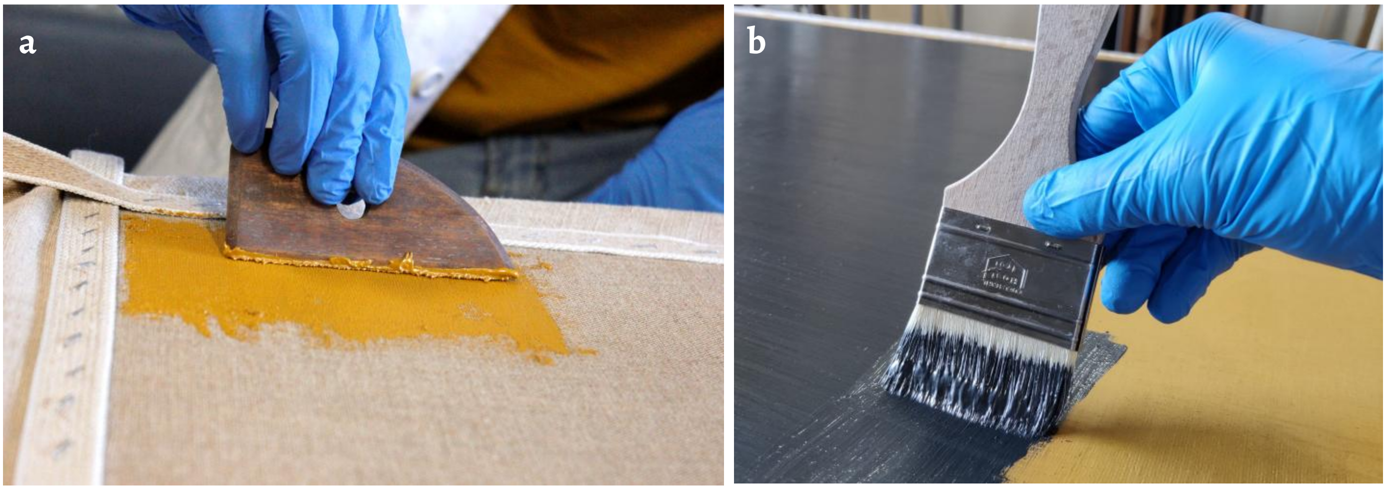


**Figure 2.** Applying: ***a)*** the ground layer consisting of ochre and lead white in linseed oil **(**the ground was applied using a spatula because of its lower amount of binder and to obtain the thinnest layer possible)**;** ***b)*** the paint layer made of lead white and carbon black in linseed oil **(**the paint layer, more fluid than the ground, was applied by brush**).**

## Reference material

For comparative purposes, Plexisol P550, a commonly used acrylic resin (N-butyl-methacrylate), was selected as the reference consolidant. Despite its differing chemical nature, this material serves as a benchmark for evaluating the performance of crystalline nanocellulose (CNC). The comparison was conducted using typical application concentrations: CNC at 0.5-2 % and Plexisol P550 at 15 % in a petroleum ether/acetone solution (80:20 ratio). This approach facilitates straightforward interpretation of the results under conditions mimicking normal use, acknowledging the inherent differences in the materials' characteristics and application methodologies (Table 2).

**Table 2.** Materials tested.

| Materials | Concentration (%) | Vehicle/Solvent | Method of application |
|---|---|---|---|
| CNC | 2 | Water | Brush |
| | 1 | Water | Brush/Nebulization |
| | 0.5 | Water | Brush |
| | 2 | Water – ethanol (1:1) | Brush |
| | 1 | Water – ethanol (1:1) | Brush/Nebulization |
| | 0.5 | Water – ethanol (1:1) | Brush |
| Klucel E | 1 | Water | Brush |
| | | Water – ethanol (1:1) | Brush |
| CNC + Klucel E 1 % | 1 | Water | Brush |
| | | Water – ethanol (1:1) | Brush |
| Plexisol P550 | 15 | Petroleum ether 80-120 ° - Acetone (80:20) | Brush |
| CNC - desulfated | 1 | Water | Brush |
| CNC – functionalized | 1 | To be evaluated | Brush/Nebulization |

## Application and testing protocols

To standardize the amount of consolidant applied, the average quantity required for complete impregnation was calculated for each material. This procedure provides a consistent basis for comparing the materials' performance and quantifying the volume required for effective application. CNC is being tested in both aqueous suspensions and hydroalcoholic mixtures to explore its variability in application (Figure 3). An alternative method, i.e., applying materials until achieving a uniform added weight, was considered but ultimately rejected due to its potential to complicate data interpretation.

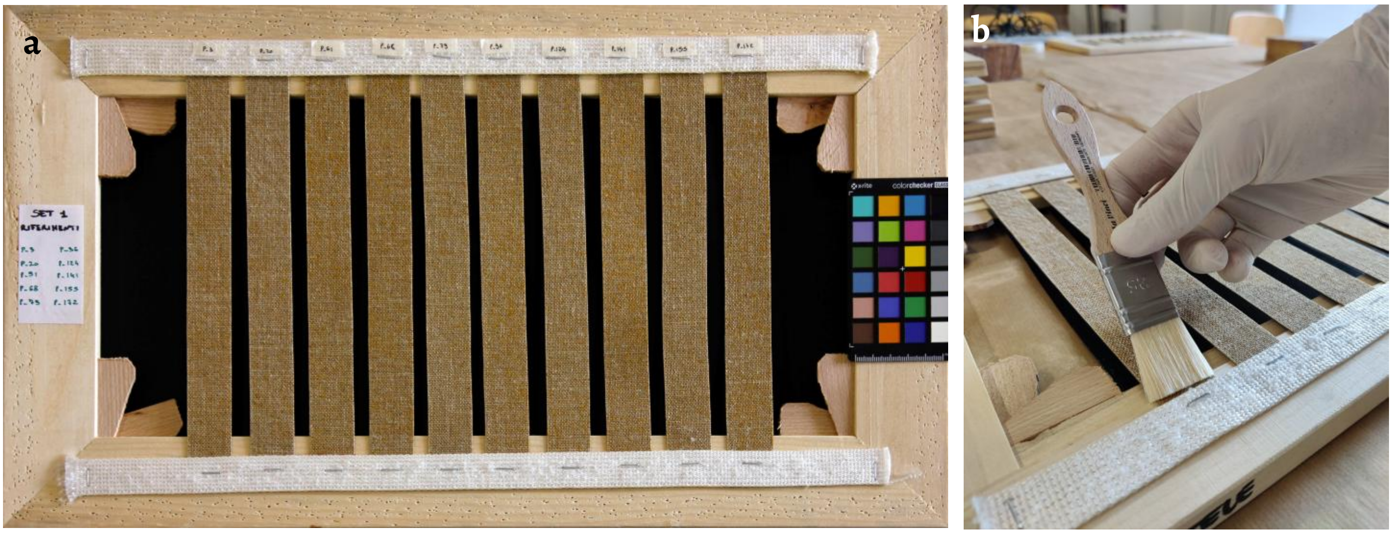

**Figure 3.** The mock-ups: *a)* applied on wooden stretchers prior to the application of the consolidants, in order to avoid deformations induced by the use of water-based materials; *b)* application of CNC.

**Evaluation parameters**

To summarize, the ongoing research project aims to address key aspects that contribute to qualifying crystalline nanocellulose as a consolidant for depolymerized cellulosic fabrics. These aspects include:

- Mechanical performance: the values of load and elongation at break, in addition to the Young's modulus, are to be evaluated through the implementation of dynamometric tests. These tests are to be conducted following the reference standard, ISO 13934-1 (2013). Dynamic mechanical analysis (DMA) will also be employed to ascertain the behaviour of treated canvases under conditions of variable humidity;
- Chemical stability will be evaluated employing pH measurements on the treated surface before and after treatment, and after artificial ageing, in order to assess any changes in the tested materials;
- Hygroscopic behaviour: the tendency of nanocellulose to absorb environmental moisture will be compared with that of other materials using hygroscopic absorption measurements;
- Optical properties and surface morphology; colorimetric measurements will be implemented to assess any variations in the appearance of the canvas before and after treatment, and also after artificial ageing. Furthermore, the impact of the various materials tested on the surface morphology will be evaluated at different scales, exploiting multiple techniques, including stereoscopic microscopy, scanning electron microscopy (SEM), and atomic force microscopy (AFM);
- Penetration into the substrate: the actual diffusion into the substrate will be assessed by comparing the results obtained by multiple microscopy techniques, e.g., stereoscopic microscopy, confocal microscopy and scanning electron microscope (SEM);
- Adhesion properties: the adhesion of crystalline nanocellulose to the canvas will be measured by making use of a methodology inferred from the recent scientific literature [9, 18-19], adequately adapted and optimized;
- Water usage: the potential for decreasing the quantity of water utilised in the CNC application process will be ascertained through the measurement of the added weight after the treatment, employing both the use of a brush and nebulisation. Furthermore, the chemical functionalization of CNC is being investigated for its capacity to allow dispersibility in apolar organic solvents.

**Table 3.** Comparison of the possible advantages and disadvantages of some of the materials in the study.

| | Plexisol P550 | Beva 371 O.F.* | CNC | CNC + Klucel E |
|---|---|---|---|---|
| Material compatibility | - | - - | + + + | + + |
| Hygroscopicity | - | - - - | + + | + + + |
| Solvent or dispersant medium | Organic solvents | Organic solvents | Water or water-ethanol mixtures | Water or water-ethanol mixtures |
| Toxicity | + + | + + + | - - - | - - - |
| Tensile strength increase | + + + | + + | + + | + + |
| Chemical stability | +/- | +/- | + + | + |
| Biodegradability | No | No | Yes | Yes |
| Aesthetic impact | - | - - - | ++ | + |
| Typical use concentration range | 10-15 % | 10-15 % | 0.2 - 2 % | 1 %** |
| Need for heat-based reactivation | Yes | Yes | No | No |
| Need for forced drying (ironing) | No | No | Yes | Yes |
| Ease of use | + + | + | - | - |
| Removability | - | - - | To be evaluated | To be evaluated |

* Data for Beva 371 O.F. were derived from a previous study and were not obtained within the framework of the present research.
** The concentration of CNC + Klucel E that was tested was 1 % for both materials (w/v), i.e. one gram of both for 100 ml of water. Legend: - - - = very low; - - = low; - = insufficient; +/- = barely sufficient; + = moderate; + + = high; + + + = very high.

At the current state of research, a preliminary overview of the potential advantages and disadvantages of the materials under study can be proposed. It should be noted, however, that several of the aspects reported are still under evaluation and may be subject to future revisions and additional considerations (Table 3). The assessments presented here must therefore be regarded as indicative, as many of the parameters involved are affected by multiple variables that limit the possibility of providing a definitive evaluation. For instance, material compatibility is a multifaceted concept, closely related to the specific stratigraphy of the artworks; likewise, the toxicity of the two synthetic materials is strongly influenced by the solvent mixture used for their dilution. The observed increase in tensile strength also appears to depend on the particular stratigraphy of the substrate to which the materials are applied. Moreover, the removability of the products is influenced by several factors and is generally only partial, since consolidation typically entails the impregnation of the substrate.

## Conclusion

The study's ultimate goal is to produce data of immediate relevance to the conservation field, enhancing the understanding of crystalline nanocellulose as an innovative, sustainable, and promising material. In order to do so, the studies known in the literature have been thoroughly reviewed, with the main results extracted and critically analysed; following, the less investigated topics have been identified. The overview of the state of the art clearly showed that the mechanical performances of the material have already been validated through multiple studies, although a significant proportion of these focus on cotton fabrics, which are less pertinent in the context of utilising nanocellulose on ancient paintings. In addition, given the extreme technical variability relating to canvas painting, it is considered that the repetition of appropriate tests carried out according to the reference standard, but on linen mock-ups, characterized by a different stratigraphy, may provide useful data to clarify this crucial aspect further. Also, an objective of these tests is to make a comparison between different kinds of products, e.g., CNC made in a laboratory and a "commercial" one, and also specific kinds of the same material, with other properties.

Concerning the aspects that require further study, these have been identified in the fundamental themes of the diffusion of the material in the substrate, its adhesion to it, and the use of water for its application. These issues have been addressed only in a limited number of scientific publications, despite their practical significance, even though they directly influence the applicability of nanocellulose to paintings. Hence, the primary objective of this study is to provide relevant data in the field of canvas paintings conservation, with a focus on the potential and limitations of CNC. The results of the study will offer new insights about CNC behaviour and clarify the possibility of its use also on previously lined paintings. By doing so, the aim is to encourage the informed use of this innovative, eco-friendly, and more compatible material in art conservation.

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