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Contemporary applications of cellulose derivatives in conservation and restoration of paper, wood, textiles and painted cultural heritage

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This review assesses the application of cellulose derivatives, specifically cellulose ethers and nanocelluloses, in cultural heritage conservation. By analysing literature and case studies, it highlights how their unique properties enable eco-friendly and effective treatments—such as reinforcement, deacidification, bacteriostasis, and colour fixation—for paper, wood, oil painting, and textile artefacts. These applications are shown to align with the critical conservation tenets of reversibility and minimal intervention.

Cellulose derivatives and their properties

Cultural heritage, as carriers of historical and cultural heritage, bear invaluable information about the development of human civilisation. Their conservation and restoration efforts hold profound significance for the transmission of cultural heritage. With advances in materials science, the application of natural polymeric materials in heritage conservation has garnered considerable attention. Cellulose and its derivatives stand out due to their unique properties. Cellulose is a polymeric compound formed by D-glucose units linked via $\beta(1-4)$ glycosidic bonds, exhibiting a degree of polymerisation up to 18,000 and molecular weights reaching the 10⁶ order of magnitude¹. It is a natural polymer present in numerous plants and abundantly available in nature. Cellulose possesses highly crystalline molecules and hydrogen bonds formed through its molecular chains. This endows it with high strength and Young's modulus, making it a material of choice for diverse applications, including composites, high-performance materials, and functional applications². Driven by heritage conservation demands, research into cellulose derivatives has deepened. Among these, cellulose derivatives have emerged as novel conservation materials due to their advantages: renewability, abundance, biocompatibility, relative stability³, high Young's modulus, low density, and high tensile strength^{4–6}. Research into the application of cellulose derivatives in cultural heritage conservation and restoration not only provides green, efficient material solutions for heritage preservation but also expands the application boundaries of cellulose materials, aligning with the dual demands of cultural heritage conservation and sustainable development. This paper, therefore, focuses on the application of cellulose adhesives and nanocellulose in cultural heritage conservation. In the field of cultural heritage conservation and restoration,

cellulose gum and nanocellulose, as green and renewable materials, not only possess good biocompatibility and environmental benignity but also show potential for retreatability. This aligns with the conservation principles of “minimal intervention” and “reversibility”, and they are now applied in the conservation and restoration of numerous paper, wooden, and textile artefacts, as shown in Tables 1 and 2.

Types and properties of cellulose adhesives

Cellulose adhesives are produced by reacting cellulose with certain reagents to replace the hydroxyl groups at the C2, C3, and C6 positions of glucose. Commercially available cellulose adhesives primarily include: sodium carboxymethyl cellulose (CMC), methyl cellulose (MC), ethyl cellulose (EC), methyl ethyl cellulose (MEC), hydroxyethyl cellulose (HEC), hydroxypropyl cellulose (HPC), and microcrystalline cellulose (MCC) derived from specially treated cellulose⁷. Among these, water-soluble polymers featuring a cellulose backbone and ether groups containing substituents are produced by chemically modifying cellulose with concentrated sodium hydroxide, followed by reaction with one or more etherifying agents such as chloroform, chloroethane, ethylene oxide, or propylene oxide. These are termed cellulose ethers, encompassing CMC, EC, HEC, HPC, MC, ethyl hydroxyethyl cellulose (EHEC), hydroxyethyl methylcellulose (MHEC), and hydroxypropyl methylcellulose (HPMC)^{8,9}.

According to the different substituents on the molecule obtained from the etherification reaction, it can be divided into single ethers and mixed ethers. Single ether refers to the etherification product that only introduces one type of substituent into the cellulose molecule, and its chemical properties and functions are mainly determined by the structural characteristics

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Table 1 | Application of cellulose adhesives in cultural heritage conservation

Cellulose adhesives	Application	Utilisation	Mechanism	References
EC	Consolidation of paper-based cultural heritage	EC and nano-SiO ₂ composite	Forming a coating film on the fibre surface and filling pores while preserving the fibre mesh structure, thereby enhancing tensile strength	37
CMC	Consolidation of paper-based cultural heritage	β -cyclodextrin (β -CD) grafted onto CMC	Epoxy chloropropane (ECH) serves as the cross-linking agent, grafting β -CD onto CMC. This combines CMC's film-forming properties with β -CD's inclusion capability	39
	Antimicrobial treatment for paper-based cultural heritage	Using CMC as the base material, a composite protective solution of TMP-DCMC-BBR was synthesised via Schiff base reactions with diacetyl carboxymethyl cellulose (DCMC), trimethoprim lactate (TMP), and aminobarrimin (BBR-NH ₂).	The cationic structure of BBR binds to negatively charged components (e.g., phospholipids) on bacterial cell membranes, disrupting them. TMP inhibits nucleic acid and protein synthesis. The carboxymethyl and hydroxyl groups on CMC molecular chains uniformly disperse BBR and TMP through hydrogen bonding and electrostatic interactions	62
	Adhesion of textile cultural heritage	7% CMC (weight-to-volume ratio) in deionised water solution + trace acetone	CMC forms strong hydrogen bonds with polar groups on the surfaces to be bonded	96
HEC	Consolidation of wooden cultural heritage	0.5% HEC (by weight) in ultrapure water solution	HEC forms dense hydrogen bonds with the polar groups of the wood matrix via hydroxyl groups	70
HPC	Consolidation of paper-based cultural heritage	Composite system of magnesium oxide (MgO)-loaded halloysite nanotubes (Hal) with HPC	Hal releases MgO to neutralise paper acidity, while HPC forms a continuous film filling inter-fibre voids, synergistically enhancing inter-fibre bonding strength.	38
	Consolidation of wooden cultural heritage	70% ethanol solution of 3% HPC (mass percentage) + 30% solution of 2% CNF (volume ratio)	CNFs form a network structure within the HPC matrix, enhancing stress transfer efficiency, while their nanoscale dimensions ensure effective filling of wood pores	72
MCC	Adhesion of wooden cultural heritage	APTES grafted onto MCC to prepare amine-functionalised cellulose (AC), subsequently crosslinked with branched epoxy compound EAGE ₄	The reaction between AC's amino groups and EAGE ₄ 's epoxy groups enhances adhesive cohesion. Simultaneously, unreacted epoxy groups in the adhesive react with amino groups on APTES-modified wood surfaces. During hot pressing, the adhesive permeates wood pores and cures, achieving mechanical interlocking.	85
HEMC	Consolidation of oil paintings and textile heritage	Silanized HEMC/NCC (HEMC concentration 2 wt%, NCC volume fraction 4.5%) and MgO deacidifier were dispersed in heptane and evenly applied to the back of the canvas by brushing	HEMC as the matrix in the heptane volatilisation to form a continuous film, with NCC to form a rigid network, the use of NCC with high surface area to enhance the interfacial bonding between the fibres, to enhance the mechanical strength.	97
HPMC	Consolidation of oil paintings and textile heritage	3.5 wt%–6 wt% HPMC ultrasonic atomization, for extremely fragile oil painting substrates, 1–2 applications to stabilize micro-flaking. 2.5%–5 wt% HPMC pneumatic atomization, for a slightly larger range of paintings, can be combined with ethanol–water pre-atomization to enhance penetration.	ULV-HPMC realises the reinforcement of the substrate through physical adsorption and intermolecular forces. The hydroxyl group and methoxy group in its molecular structure form a hydrogen bond with the hydroxyl group on the surface of pigment particles, meanwhile, the cellulose ether chain can entangle the pigment particles to enhance the cohesion and adhesion between the particles.	98

Table 2 | Application of nanocellulose in cultural heritage conservation

Nanocellulose	Application	Utilisation	Mechanism	References
CNF	Consolidation of paper-based cultural heritage	CNF blended with polyvinyl alcohol (PVA) and nano-silica (MPSNP) with PVA	CNF forms hydrogen bonds with the hydroxyl groups of paper cellulose fibres, whilst simultaneously cross-linking with PVA to form a network, enhancing inter-fibre bonding	36
		Blending of cotton cellulose nanocrystals (CNC-C) and cotton cellulose nanofibrils (CNF-C)	Fully released hydroxyl groups in CNC-C and CNF-C enhance hydrogen bonding capacity. The long fibrillar network of CNF-C fills voids while rod-like whiskers of CNC-C intercalate, synergistically stabilising paper fibre fractures or gaps	35
	Adhesion of paper-based cultural heritage	CNF blended with wheat starch-based adhesive	Hydroxyl groups on CNF surfaces interact with wheat starch micelle molecules via hydrogen bonds, whilst the nano-mesh structure of CNF encapsulates starch granules and restricts their molecular chain movement.	48
	Antimicrobial properties of paper-based cultural heritage	CNF undergo ultrasonic self-assembly to form composites with carbon nanoparticles (CNPs), which are subsequently blended with PVA	The filamentous structure of CNF provides a three-dimensional support network for CNPs, facilitating easier contact between the antibacterial active sites of CNPs and bacteria. This enables electrostatic adsorption between the negative surface potential of CNPs and bacteria	60
	Consolidation of wooden cultural heritage	Blending CNF and CNC	The high aspect ratio of CNF readily forms network structures, enhancing mechanical properties. Unmodified CNC strike a balance between reinforcement efficiency, ductility, and transparency, rendering them excellent reinforcing fillers.	71
		70% 3% HPC (mass percentage) ethanol solution + 30% 2% CNF (volume ratio) solution	CNFs form a network structure within the HPC matrix, enhancing stress transfer efficiency, while their nanoscale dimensions ensure effective filling of wood pores	72
	Adhesion of wooden cultural heritage	Synergistic interaction between CNF and lignin soybean protein isolate (SPI)	CNF form multiple hydrogen bonds via hydroxyl groups with SPI's amino and carboxyl groups and with phenolic hydroxyls in lignin, while lignin binds to SPI's hydrophobic regions through hydrophobic interactions	86
CNC	Adhesion of paper-based cultural heritage	Potato starch-based adhesive + CNC	CNC physically fill large pores formed during starch expansion; both potato starch and CNC exhibit negative charge in alkaline aqueous solutions. When starch pores collapse, like-charge repulsion inhibits complete collapse, promoting collisions and reactions between starch molecules and reactive ions, thereby advancing oxidation or cross-linking reactions	47
	Deacidification of paper-based cultural heritage	Combining CNC with CaCO ₃ particles via chemical vapour deposition (CVD)	Establishment of CaCO ₃ alkaline neutralisation and alkaline reserve; synergistic effect of CNC dispersion and carrier	54
		Oleic acid grafted onto the CNC surface, incorporating Ca(OH) ₂ and CaCO ₃	Succinic acid successfully grafted onto CNC, imparting excellent dispersibility; Ca(OH) ₂ and CaCO ₃ neutralise acidic substances	57
	Antimicrobial properties of paper-based cultural heritage	CNC + polyhexamethylene guanidine (PHMG)	As a cationic polymer, PHMG's positively charged molecular chains undergo electrostatic adsorption with negatively charged microbial cell membranes, disrupting fungal cell membranes. It uniformly distributes across surfaces to form a sustained antimicrobial barrier, while CNC fill fibre pores to create a dense network	61
	Adhesion of wooden cultural heritage	PVA wood adhesive + CNC	CNC enhance PVA's adhesive strength. Their 150–250 nm rod-like structure forms a network within PVA, improving mechanical properties and thermal stability through nano-reinforcement and network formation.	87
	Consolidation of oil painting canvases	3% CNC (weight-to-volume ratio) applied in three coats	Following three coating applications, CNC—as short rod-shaped nanoparticles—form a continuous, dense film layer on aged canvas surfaces. Hydroxyl groups on the CNC surface form hydrogen bonds with hydroxyl groups in the canvas cellulose, thereby strengthening inter-fibre bonding.	91

of the single substituent, such as hydrophobicity, hydrophilicity, ionicity, and can be further subdivided into three categories according to the chemical class of the substituent, among which the alkyl ether is generated by the reaction between cellulose hydroxyl group and alkylation reagent, and the molecular structure only contains alkyl substituents, and the common types include ethyl. The common types include EC, Propyl Cellulose (Propyl Cellulose), Phenyl Cellulose (Phenyl Cellulose) and Cyanoethyl Cellulose (Cyanoethyl Cellulose), etc. EC is one of the most widely researched and applied varieties of this category, and its performance is highly dependent on the degree of substitution (DS), with low DS (0.8–1.7). EC with low DS (0.8–1.7) is soluble in water, but due to the difficulty of controlling the ethylation reaction, there are fewer commercialized products, while EC with high DS (2.4–2.8) shows excellent solubility in organic solvents, which is soluble in chloroform, dichloromethane and mixed solvents of methanol and ethanol, and possesses good film-forming and oil resistance, but there are significant shortcomings in long-term stability of EC with high DS, which is easy to form peroxides under the conditions of heat (90–110 °C) or light exposure, and easy to form peroxides under the conditions of heat (90–110 °C) or light exposure. However, the long-term stability of EC of DS has significant defects, and it is easy to form peroxide under heat (90–110 °C) or light exposure, which triggers molecular chain breakage and discolouration. Hydroxyalkyl ethers are prepared by reacting cellulose with epoxy alkane reagents, and the substituent group is the alkyl chain containing a hydroxyl group. Typical representatives of HEC and HPC, and the key feature of this type of ether is the synergistic effect of molar substitution (MS) and DS. In the case of HEC, for example, when ethylene oxide reacts with cellulose, the newly generated primary hydroxyl group is easier to further react than the original secondary hydroxyl group of cellulose to form polyoxyethylene side chain, so the MS can be much higher than the DS effect is very small, and the HPC can be solved in polar organic solvents such as ethanol due to the hydrophobicity of hydroxypropyl group. Carboxy alkyl ether substituent for the polar chain containing carboxyl group, its representative varieties of CMC, CMC's core properties stem from its ionic structure, the presence of carboxyl group so that its aqueous solution has good stability and thickening, and solubility is not subject to the dramatic impact of DS (0.4–1.4), even if the DS is low as 0.4, the sodium salt of the form of CMC can be completely soluble in water, and in addition, the equilibrium water content of CMC is significantly higher than that of other fibres, and the water content is much higher than that of other fibres. The equilibrium water content of CMC is significantly higher than that of other cellulose ethers. In terms of long-term stability, CMC has excellent performance, after heat ageing at 90 °C for 500 h, the loss of characteristic viscosity is only 5–8%, which is much lower than that of HPC, with a loss of more than 50%. Mixed ethers refer to etherification products in which two or more different substituent groups are introduced into the cellulose molecule at the same time, and the synergistic effect of different substituent groups realises “functional complementarity” in their performance. Its performance can be realized through the synergistic effect of different substituents to achieve “functional complementarity”, which can be targeted to solve the limitations of a single ether, such as the balance of water solubility and temperature resistance, stability and film-forming optimization, common varieties include EHEC, hydroxyethyl methyl cellulose (MHPC) and hydroxypropyl methyl cellulose (MHPC), of which EHEC contains both ethyl and hydroxyethyl substituents, and EHEC contains both ethyl and hydroxyethyl substituents. EHEC contains both ethyl and hydroxyethyl substituents, according to the ratio of the two substituents can be divided into two categories of water-soluble (WS-EHEC) and organic soluble (OS-EHEC), MHPC with methyl and hydroxypropyl as a mixture of substituents, the core of its performance lies in the regulation of methyl DS and hydroxypropyl MS, compared with the pure MC, the thermal gel temperature of MHPC is higher, up to 90 °C is suitable for the temperature-sensitive artefacts of the restoration scene. Restoration Scenarios^{3,10,11}

In terms of reversibility, cellulose ethers have good water solubility due to the presence of polyhydroxyl groups, and have different solvent choices for organic solvents depending on the substituent groups. For example, MC

can be removed by water immersion, EC needs to be removed with the help of organic solvents such as ethanol, and MHPC can still maintain good solubility in specific solvents to achieve reversible operation, but it should be noted that some highly substituted ethers, such as EC, may have decreased solubility due to the cross-linking of molecular chains after long-term ageing, and it is difficult to remove the traces of residue completely [Adhesive Compendium for Conservation]^{12–14}.

The viscosity properties of cellulose gum were significantly correlated with its concentration, DS, substituent distribution, molecular type and degree of polymerisation, DP. In terms of concentration dependence, as the concentration of cellulose gum increases, the number density of molecular chains in the system increases, and the probability of physical entanglement between molecular chains increases significantly, which leads to the enhancement of intermolecular intermolecular van der Waals force, hydrogen bonding and other interactions, and macroscopically manifests itself as a sustained increase in viscosity, which directly confers excellent adhesion and thickening properties to cellulose gums to make them suitable for different protection scenarios, such as paper reinforcing and textile adhesive bonding. This change in viscosity directly gives cellulose adhesives excellent bonding and thickening properties, making them suitable for paper reinforcement, textile bonding, and other protection scenarios. From the molecular determinants of solubility and viscosity, cellulose ether exists in water in a colloidal dispersion state, and the core of its viscosity depends on the degree of polymerization (DP), the higher the DP, the longer the length of the molecular chain, and the stronger the degree of intermolecular entanglement and interaction, the higher the solution viscosity accordingly; at the same time, the degree of DS and the distribution of substituent groups indirectly regulate the viscosity characteristics by influencing the polarity and spatial configuration of the molecular chain, for example, CMC with high DS has a high degree of viscosity and a high degree of spatial configuration. For example, high DS CMC is easier to form stable colloidal system than low DS species under the same DP because of the appropriate density of polar groups in the molecular chain, and the viscosity response to changes in concentration is more significant; and different molecular types due to the substituent type and combination of differences in the degree of stretching of the molecular chain in the process of colloidal solubilization, which also leads to differences in viscosity under the same DP and concentration.^{12,14}

Cellulose gum has better film-forming properties. Cellulose ethers have high mechanical strength, flexibility and heat resistance, and good compatibility with various resins and plasticisers, which can be used in the manufacture of plastics, films, adhesives, latexes, coating materials for medicinal dressings, building adhesives for construction, tackifiers and film-formers in coatings, and coated adhesives in the paper industry, etc.¹⁵. For example, films made of high viscosity and high molecular mass CMC have high strength and flexibility. The use of certain water-soluble resins as crosslinking agents and CMC formulated into a mixed solution, made of film by drying and plasticising treatment, that becomes insoluble in water products¹.

Types and properties of nanocellulose

Nanocellulose refers to cellulose with nanometre diameter and high aspect ratio, which has excellent properties of nanomaterials, such as high specific surface area, low density, and high strength¹⁶, and it has at least one dimension with spatial dimensions in the range of 1–100 nm, including cellulose nanofibers (CNF), cellulose nanocrystals (CNC), and bacterial nanocellulose (BNC)¹⁶. Among them, CNCs are usually prepared by acid hydrolysis of cellulose materials dispersed in water. Concentrated sulfuric acid is generally used to dissolve the amorphous regions of cellulose, and the crystalline regions are left alone¹⁷, which consists of almost 100% cellulose with a high degree of crystallinity (54–88%)². The rod-like nanoparticles obtainable by mechanical or ultrasonic dispersion typically have a length ranging from 200 to 500 nm and a diameter ranging from 3 to 35 nm, CNCs have an axial Young's modulus of 140–160 GPa and an axial tensile strength of 8–10 GPa, this value is much higher than that of conventional polymers, originating from the CNC. This value is much higher than that of

conventional polymers, which is due to the orderly arrangement of glucose units inside the crystal and the strong hydrogen bonding. The transverse modulus is significantly lower than axial, 15–30 GPa; the transverse tensile strength is only about 1 GPa, and the bulk modulus is 5–6 GPa, reflecting that the deformation resistance of CNC is weak under three-dimensional pressure, which is related to the densification of the crystal structure. The refractive index of CNC is lower (1.46–1.49), so its thin film is much higher than that of conventional polymers. 1.49), so its films show transparency, but if aggregation occurs, it will lead to a decrease in transmittance due to light scattering, and the charged CNC will self-assemble in concentrated dispersions to form a chiral nematic liquid crystal structure, which exhibits an obvious birefringence phenomenon^{18,19}.

CNC hydrolysed by sulfuric acid with sulfonic acid groups on the surface, its aqueous dispersion can be maintained stable by electrostatic repulsion for several weeks without significant settling²⁰. The porosity and permeability of CNC are related to the particle stacking mode and interfacial adsorption structure, if the concentration of CNC increases or the surface charge decreases, the porosity will increase, and the permeability depends on the stacking density of CNC, at low concentration CNC is dispersed, and the pores in the layer are large, which makes it easy for gases or liquids to penetrate; at high concentration, CNC forms a dense network, and the permeability decreases significantly. At high concentrations, CNC forms a dense network, and the permeability decreases significantly²¹.

CNF are long entangled fibres with diameters in the nanometre range, produced from cellulose pulp suspensions by high-pressure milling, and form a strongly entangled network of nanofibers²², CNF have diameters of 5–50 nm and lengths of a few micrometres²³, and aspect ratios as high as 60–100, and a high aspect ratio confers CNF with a very low percolation threshold, and thus it has good ability to form a continuous network in a filled liquid medium or polymer. The ability to form a continuous network in filled liquid media or polymer matrices is excellent, and the thin films formed by the dilute dispersion system of CNF are more densely structured and optically semi-transparent; the transparency of these films at 600 nm is about 72%. After additional polishing, the transmittance of the CNF films was improved to 78–90%. The axial modulus of single CNF was 29–36 GPa, the axial tensile strength was 0.8–1 GPa, and the tensile strength of the CNF films was 170–230 MPa with an elongation at break of 5–7%. The axial modulus and tensile strength of the CNF varied with the MFA (angle between microfibril filament and axial direction), increasing and decreasing significantly, when MFA increases from 0° to 30°, axial modulus decreases from about 40 GPa to 10 GPa, and tensile strength decreases from 1 GPa to 0.2 GPa. The MFA of actual CNF is usually 10–12°, and it is the main reason why their mechanical properties are lower than the theoretical values¹⁹. CNF were prepared using a mechanical method so that the cellulose chains are broken by force in the longitudinal axis, thus extracting nanocellulose²⁴. The CNF prepared under this method has less cellulose chain breakage in the amorphous region, so the CNF have a larger aspect ratio and better flexibility²⁵. Unmodified CNFs are prone to gradual agglomeration due to the easy formation of hydrogen bonds on the surface hydroxyl groups and storage after conventional drying. Modified CNF, such as carboxymethylation, have increased negative surface charge and electrostatic repulsion can inhibit agglomeration in long-term storage, and their aqueous dispersions can be stabilised for several weeks²⁰. The porosity and permeability of CNF are dependent on the structure of the fibril network and the ability of the interface to form gels, and the permeability of the fibril network decreases with salt concentration and can be regulated in complex with polymers²¹.

BNC is a cellulose with high chemical purity and polymerisation, excellent mechanical properties, a relatively environmentally friendly production process and good biocompatibility²⁵. BNC is usually produced by bacteria, and during the biosynthesis of BNC, glucose chains are supplied in the body of the bacterium and excreted through small pores in the cell wall. When glucose binds to the cell wall, ribbons of bacterial CNF are formed, and this ribbon-like mesh structure produces a unique nanofibrous system of 20–100 nm in length, with long and thin fibrils intertwined to form a

three-dimensional porous network. A single BNC has an MFA of only 1–3°, and its axial modulus is 80–110 GPa, its axial modulus is 80–110 GPa, axial tensile strength is 1.5–1.7 GPa, which is close to the mechanical level of CNC, and it is the type of natural nanofibrillar cellulose with the highest mechanical strength. The dry film formed by interwoven BNC filaments has lower mechanical strength than monofilaments, with a modulus of 10–30 GPa, tensile strength of 200–250 MPa, and elongation at break of 64%. Although a small amount of voids exists in the interwoven network of filaments in the BNC film, the high crystallinity and low MFA still make its mechanical properties superior to those of CNF film^{19,23}. The smaller size of the BNC fibre bundle and the dense network reduce light scattering, resulting in better BNC phototransparency. BNC remains regular for a long period of time in dry or wet conditions, and when stored at room temperature (25 °C) and 60% humidity, the porosity (60–80%) and filament size of BNC do not change significantly over time, which results from the structural stability of its naturally occurring strong hydrogen bonding network²⁰.

All three types of nanocellulose can coexist well with biological systems without obvious toxic reactions and can be safely used in medical dressings, food packaging and other scenarios. Surface hydroxyl groups provide active sites for chemical modification, whether CNC, CNF or BNC, and can be introduced into the functional groups through esterification, etherification, grafting and other reactions²⁶. Oxidatively modified nanocellulose can introduce carboxyl groups on the surface, which helps to improve the hydrogen bonding capacity between molecular cellulose and increase the adhesive strength between fibres²⁷. There is also graft copolymerization modification, which utilises the reactive hydroxyl groups on the cellulose molecular chain as reaction sites to achieve cellulose modification²⁸, resulting in the formation of polymer chains with unique properties in nanocellulose. Representative nanocellulose modifications for conservation and restoration of cultural heritage include three types in the NanoForArt project that revolve around the cleaning, consolidation, and deacidification needs of cultural heritage conservation, one is nanoparticle surface modification, such as functionalized modification of inorganic nanoparticles such as silicon dioxide and calcium hydroxide with silane coupling agent to enhance compatibility and adhesion, and the other is nanostructured cleaning fluid modification. The second is nano-structured cleaning fluid modification, by regulating the oil-water-surfactant ratio of microemulsion and introducing co-surfactant to optimise the decontamination; the third is substrate suitability modification, adjusting the viscosity of nano-dispersions and drying rate for inorganic substrates, such as stone and mural, in order to improve the permeability, and alkaline or antimicrobial modification of nano-particles for organic substrates, such as paper, wood, etc., in order to avoid degradation, and so on.

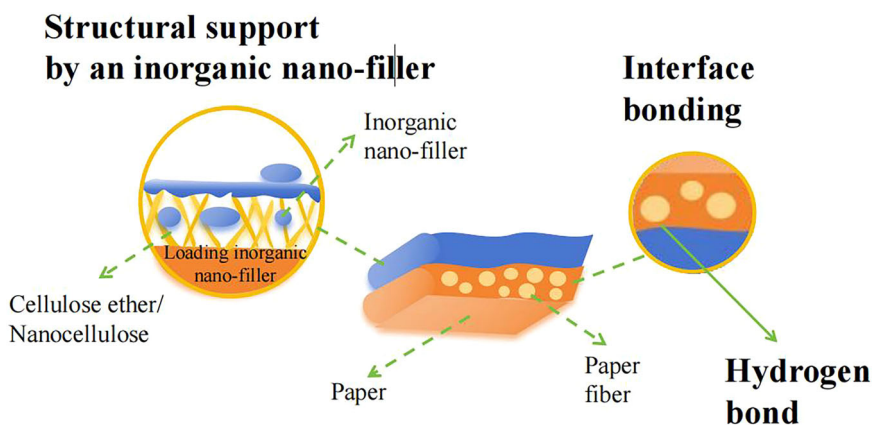
Application of cellulose derivatives in the conservation and restoration of paper-based cultural artefacts

Consolidation

The conservation of paper-based cultural artefacts remains a vital component within the heritage sector. Paper degradation mainly stems from two processes: acid hydrolysis of β -D (1–4) glycosidic bonds and oxidation of β -D-pyranose glucose²⁹. Cellulose ethers and nanocellulose have long been employed in the conservation and restoration of paper artefacts, with cellulose ethers (MC) utilised as adhesives and consolidants for paper conservation as early as the 1970s³⁰.

In recent years, several high-impact reviews have emerged in the field, laying the foundation for the research framework of nanocellulose in paper protection. For example, Marques systematically summarised the performance differences and application paradigms of CNC, CNF, and BNC in paper reinforcement, deacidification, and antimicrobial scenarios, clarifying the cost advantages of CNC for scale-up reinforcement, the structural potential of CNF for film-forming restoration, and the biocompatibility uniqueness of BNC for fine treatment of paper artefacts³¹. Fomari, on the other hand, the paper focuses on three types of nanocelluloses, whose structural and property differences determine the relevance of application

Fig. 1 | The three-dimensional network of “paper fibre-inorganic nanomaterials-cellulose derivatives”. This work is licensed under CC BY-NC-ND 4.0. This figure illustrates the three-dimensional network constructed by paper fibres, inorganic nanofillers, and cellulose ether/nanocellulose. In the diagram: the light blue layered structure represents cellulose ether/nanocellulose; the light blue particles loaded on it are inorganic nanofillers. These two components work together to provide structural support for paper fibres (the tan main structure). Paper fibres, inorganic nanofillers, and cellulose ether/nanocellulose achieve interfacial bonding via “hydrogen bonds” (represented by the yellow dots and the bonding interaction in the interface area in the figure).



scenarios³². These review results consolidate the direction of the field at the macro level, while the specific research cases further refine the feasibility of the technology on the ground.

Both classical macromolecules and modern nanofibrillated cellulose can be used individually or in combination as reinforcement of paper artefacts. Different surface functionalization when used alone is one of the factors influencing the effectiveness of nanocellulose consolidation Operamolla³³. Comparison of the reinforcement effects of two different surface-functionalized CNC. Sulfated CNC prepared by sulfuric acid hydrolysis can form a uniform film between paper fibres and fill fibre gaps due to the surface sulfate groups and the repulsion of negative surface charge. Neutral CNC prepared by hydrochloric acid hydrolysis, without surface charge, are easy to agglomerate and encapsulate on the surface of single fibres to form a fibre network. The latter has no acidity effect and long-lasting mechanical reinforcement, whereas the former may need to be used in combination with a deacidifier to neutralise the acidic risk posed by its sulfate groups. The study also designed a “gellan gum hydrogel + electrochemical sensor” coupled system, in which the gellan gum hydrogel is used as a non-invasive removal carrier to adsorb CNC on the surface of paper through controlled-release water, while the coupled electrochemical system enzymatically cleaves CNC adsorbed in the gel to glucose, and then detects the concentration of glucose and generates a corresponding current signal from modified electrodes, realizing the removal of CNC. The coupled electrochemical system detects the glucose concentration by the modified electrode and generates the corresponding current signal to realise the real-time monitoring of CNC removal. Experiments showed that the system can capture the characteristic current peak of CNC removal after 400 s of gel application, which can meet the requirements of cultural heritage protection for the reversibility of reinforcement treatment.

The structure of nanocellulose with different dispersion media also affects the reinforcement effect. Perdoch³⁴, et al. investigated the influence and correlation between the NC structure and the dispersion medium on paper reinforcement properties. CNC is a multilayered fibre network structure with a wide particle size distribution, and when water is used as the dispersing medium, highly polar water enhances its hydrogen bonding with paper fibres, resulting in a high retention in paper, which in turn significantly enhances the apparent density, tensile index, and tear strength of the paper, while drastically decreasing the air permeability. Water-based CNF is a single uniform fibre; the water medium also promotes the formation of hydrogen bonding, so that it is better in improving the paper elongation and maintaining surface flatness. Mechanical properties and apparent density are not as good as CNC, but better than ethanol-based CNF. ethanol-based CNF due to the low polarity of ethanol, weakening the hydrogen bonding between the CNF and paper fibres, resulting in the NC agglomerates and retained in small quantities, the tensile index of the paper compared to the blank group decreased. The apparent density was the lowest, only the tear strength was slightly improved, and the air permeability was close to that of the blank group; the carboxylated CNF was a long rod

structure, the carboxyl groups on the surface enhanced the aqueous dispersion, but it did not increase the bonding sites with paper fibres, and the retention amount was insufficient, therefore, its effect on the paper tensile index, tear strength, apparent density, and air permeability was not significantly different from that of the blank group, and it only increased the elongation rate of the paper. Yi Xiaohui³⁵ et al., investigated the repair and reinforcement properties of cotton cellulose nanocrystals (CNC-C) and cotton cellulose nanofibrils (CNF-C) and their composites on bamboo paper, Xuanpaper and Yuanshu paper, and the reinforcing effects of the composites of 0.3% CNF-C and 0.8% CNC-C were better than that of 1.1% CMC, which was due to the use of groups such as carboxymethyl to replace hydroxyl groups on the cellulose and the The bonding force between paper fibres mainly comes from the hydrogen bond formed between the hydroxyl groups on cellulose, after the hydroxyl groups are replaced by ether or ester bonds, the number of hydrogen bonds formed between the fibres is reduced, so it can't form a better reinforcing effect. CNC-C, CNF-C, due to the full release of hydroxyl between the fibres, so that the formation of hydrogen bonding capacity is greatly enhanced, and at the same time, CNC-C's long-fibre filamentary network fills and CNC-C rod-shaped whiskers. CNC-C rod-like whisker insertion synergistically fixed the breaks or gaps in the paper fibres. However, the enhancement of the performance of this material for short-fibre paper was lower than that for long-fibre paper.

Cellulose derivatives and other nano-fillers used in conjunction with the principle of reinforcing paper is through the structural support of inorganic nano-fillers, cellulose derivatives of interfacial bonding, hydrogen bonding network synergistic reinforcement, to achieve performance enhancement, i.e., the use of nanometre inorganic materials of the nanoscale size effect of the penetration of the fibre interstices to enhance the rigidity of the physical filler or function of the slow-release, and at the same time, with the help of the cellulose gum or nano-fibrous cellulose, such as the film-forming and the At the same time, with the help of cellulose gum or nanocellulose and other film-forming properties and hydroxyl hydrogen bonding to bridge the fibres, the formation of “paper fibre - inorganic nanomaterials - cellulose derivatives” three-dimensional network shown in Fig. 1. This approach improves mechanical properties and mitigates chemical aging due to oxidation and hydrolysis.

The materials currently complexed with cellulose derivatives include SiO₂ and MgO. For example, Abdel-Hamied³⁶ et al., explored the effect of nanocomposites formed by CNF with PVA and silica nanoparticles (MPSNP) with PVA on the reinforcement of alizarin dyed paper manuscripts, and the experiments showed that the best result was obtained by treating dyed paper samples using 5% MPSNP/PVA. The colour difference of the sample treated with 5% CNF/PVA was too high, and the tensile strength and elongation values of the sample treated with 1% CNF/PVA were the lowest. This is due to the fact that although CNF has the same composition as paper cellulose and is theoretically compatible, the nanofiber structure of CNF is prone to agglomeration in the PVA matrix, resulting in poor penetration and dispersion of CNF/PVA on the surface and inside of

the paper. As well as, Ou Xiuhua³⁷ et al., investigated the feasibility of EC and nano-SiO₂ compound for the reinforcement of the 1757 Buddhist sutra "Seeing the Sutra Tongue Lectures Volume 2" by preparing an ethanol compound of 2.6% EC and 0.8% nano-SiO₂, which formed a wrapping film on the surface of the fibres and filled in the pore spaces without altering the chemical structure of the paper, preserving the fibre mesh pore structure and allowing the tensile strength is improved. The concentration range of this compound is narrow, and the concentration of EC is too high, which may reduce the flexibility of the paper, and the compatibility of the writing and printing colours is unknown. In addition, Lisuzzo³⁸ et al. designed a composite system of magnesium oxide (MgO)-loaded halloysite nanotubes (Hal) and HPC for paper artefacts reinforcement, in which Hal acts as a nanocontainer to slow-release MgO in order to neutralize the acidic nature of the paper, while HPC forms a continuous film to fill the fibre gap, and the two synergistically enhance the bonding force between the fibres. HPC, treated alone, can significantly improve the paper strength, but lacks a deacidification function. Although HPC alone can significantly improve the strength of paper, it lacks the function of deacidification, and the mechanical properties are easily attenuated under an acidic environment. After compounding MgO-Hal, the functions of deacidification and reinforcement synergistically fill the gap; MgO-elolite is easy to be agglomerated when dispersed alone, and HPC, as a dispersing medium, improves the penetration and distribution of MgO-eloliths in paper, so as to improve the efficiency of deacidification.

Graft copolymerisation modification of cellulose derivatives constitutes another approach for paper reinforcement. Li³⁹ et al. grafted 6.5% β -CD onto CMC using epichlorohydrin (ECH) as a crosslinking agent in a 5% NaOH solution, achieving a grafting rate of 45.02%. The resulting CMC- β -CD compound was successfully applied for paper conservation. Combining CMC's film-forming properties with β -CD's inclusion capability endows the material with multifunctionality. Yang⁴⁰ et al. utilised HEC as the base material. Through potassium persulfate-initiated radical polymerisation, they grafted hydrophobic methyl methacrylate monomers onto the HEC molecular chains, producing a hydrophobic-modified copolymer emulsion for paper conservation.

Adhesion

The common diseases of paper artefacts include breakage and mutilation. For this kind of disease often use repair framing technology, in which the use of polymer-bonded paper fibres to improve the mechanical strength of paper is an important means^{41,42}. Cellulose derivatives and paper artefacts are bonded mainly through hydrogen bonding and mechanical interlocking, in the cellulose derivatives containing ionic modification of the system, electrostatic adsorption can be assisted to enhance the interfacial interaction; chemical adhesion in the conservation of cultural heritage in the application of the usually limited and need to be used with caution, because it may reduce the reversibility of the restoration^{43,44}. Mohit⁴⁴ showed that strong intermolecular interactions between the cellulose substrate and the hydroxyl groups abundant in the derivatives through hydrogen bonding, as well as physical entanglement of the molecular chains, further strengthened the adhesion, and that these interactions resulted in a stable bond without the need for permanent chemical modification. Electrostatic adsorption only plays a complementary role in ionically modified cellulose derivatives through surface charge differences, whereas chemical bonding is not a preferred adhesion strategy for cultural heritage protection due to the risk of reversibility.

Adhesives employed in the restoration of paper artefacts must not damage the paper, while also ensuring that the restored paper remains supple and flat, resisting deformation, discolouration, insect infestation, mould growth, and moisture absorption. Additionally, the adhesive must exhibit chemical stability⁴⁵. Due to its exceptional properties, nanocellulose has seen increased application in research concerning the adhesion and restoration of paper artefacts. The incorporation of nanocellulose enhances the performance of oxidised starch adhesives⁴⁶. For example, CNC can be used as an additive in potato starch-based adhesives. CNC have high surface

energy and diffusion rate due to their small particle size, large specific surface area, and high surface group activity, which can enter into large pores formed by starch expansion, and realize intense interactions between particles and other particles by means of intermolecular van der Waals forces to accomplish the physical filling; on the other hand, potato starch and CNC are negatively charged in alkaline aqueous solution. On the other hand, potato starch and CNC are negatively charged in alkaline aqueous solution. When the starch pores collapse, the same-sex charge repulsion inhibits the complete collapse of the pores, maintains the large surface area and pore structure, promotes the collision and reaction of starch molecules and reactive ions, and promotes the oxidation or cross-linking reaction, which can maintain the stability of the microscopic dispersed structure without obvious phase separation, and realizes the homogeneous compatibility of the two at the microscopic level. From the long-term preservation standard, the viscosity retention rate of the compound adhesive after thermal aging is more than 85%, and the bond strength decreases by less than 15%; in the humid-heat aging environment, its elongation at break retention rate is more than 70%, which proves that the compound adhesive is still able to maintain the stability performance in the long-term high temperature and high humidity environment⁴⁷. Yong Qi⁴⁸ conducted comparative studies on the properties of CMC, CNF, and wheat starch paste. Findings revealed that when CNF and wheat starch-based adhesives were blended at volume ratios of 4:6 or 5:5, the composite adhesive exhibited optimal stability, film-forming ageing resistance, tackiness, and adhesion strength, flexibility and thickness of the composite adhesive film, and mould resistance of the composite adhesive solution. CMC exhibited favourable adhesion properties only at high concentrations but demonstrated poor ageing resistance.

For cellulose ether adhesives, MC is often used for edge reinforcement of paper-based cultural heritage. Its advantage lies in the ability to adjust the working time during the restoration process while reducing the impact on the original appearance of the paper. HPC is suitable for the filling and glueing processes of cultural heritage, which can improve the rheological properties of adhesives and their permeability to paper fibres, preventing the paper from becoming brittle after restoration. CMC, due to its excellent water solubility and film-forming property, is often used as a low-concentration adhesive for local reinforcement of fragile paper documents, and its viscosity can be adjusted to adapt to paper of different thicknesses. HEC, EHEC, MHEC and MHPC are mostly selected based on the balance between flexibility and permeability required for restoration. For instance, HEC can enhance the water resistance of the restoration layer, EHEC is suitable for canvas paper cultural heritage that needs to balance flexibility and adhesion, while MHEC and MHPC differ in their substituents. It is often used in multi-process repairs where high viscosity stability is required. Due to its strong hydrophobicity, EC was once used in the restoration of paper cultural heritage that required moisture-proofing in the early days. However, its application decreased later due to disputes over stability. After artificial ageing, the weight loss of MC, CMC and some MHPC can be ignored, and there is no obvious discolouration. However, the stability of EC, EHEC and some HPC varies. Some studies show that EC is prone to embrittlement during long-term storage, and EHEC is easily affected by humidity, leading to the failure of the bonding layer³. Overall, the functional differences of adhesives mainly stem from the types and quantities of substituents. By regulating the substituents, the viscosity, water solubility, flexibility and permeability of the adhesives can be customised to meet the restoration needs of different paper-based cultural heritage. Bonet et al.⁴⁹ analysed the degree of DS and degree of polymerisation (DP) of various cellulose ethers, including CMC, MC, and HPC. They found that low DS favours stronger adhesion formation, while high DP reduces adhesive consumption. The number of unsubstituted hydroxyl groups in cellulose ether molecules increases as DS decreases. These hydroxyl groups can form additional intermolecular hydrogen bonds with hydroxyl groups in paper fibres. This hydrogen adhesion enhances the adhesive strength between the adhesive and paper, thereby increasing tensile resistance. A high DP implies longer cellulose ether molecular chains and stronger intermolecular entanglement, enabling the formation of a stable network structure at lower

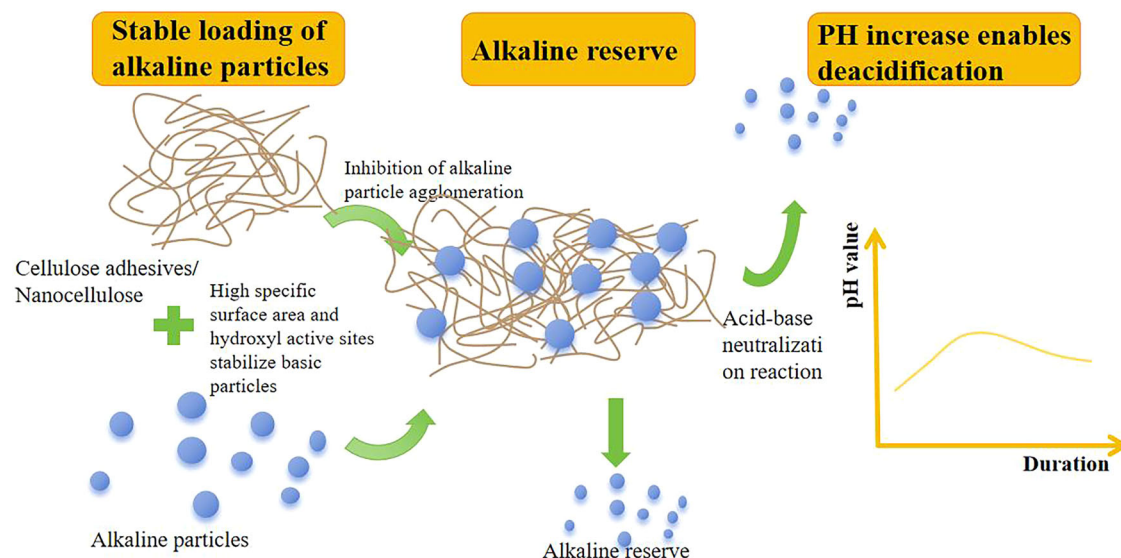


Fig. 2 | Schematic diagram of deacidification for paper cultural heritage with cellulose adhesives/nanocellulose. This work is licensed under CC BY-NC-ND 4.0. This figure illustrates the cellulose-based deacidification process for paper cultural heritage, which comprises three core segments. For the stable loading of alkaline particles, the tan fibrous structure refers to cellulose adhesives/nanocellulose, while the light blue small dots represent alkaline particles; cellulose adhesives/nanocellulose, leveraging their high specific surface area and hydroxyl active sites, inhibit the agglomeration of alkaline particles to achieve stable loading of these particles.

Regarding the alkaline reserve, the cellulose system loaded with alkaline particles adheres to the paper (the light grey substrate), forming an “alkaline reserve” (the gradually released light blue small dots in the figure). As for pH increase enabling deacidification, the alkaline reserve raises the paper’s pH value through acid-base neutralization reactions (such as the reaction between zinc oxide and carboxyl groups); in the curve on the right, the horizontal axis stands for duration, the vertical axis represents pH value, and the trend of the curve reflects the rise in pH over time, which corresponds to the deacidification effect.

concentrations. This structure provides the cohesive force required for effective adhesion. These findings offer valuable guidance for selecting adhesives in cultural heritage conservation.

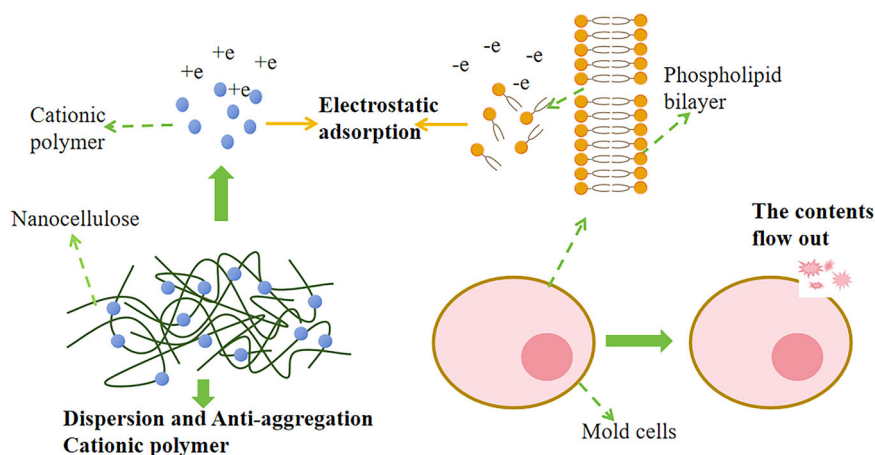
Deacidification

Acidic substances and fungal secretions cause fibre hydrolysis and paper deterioration in paper artefacts, posing a common challenge in conservation and restoration. Removing acidic compounds to neutralise the acid-induced degradation of paper fibres and prolong the lifespan of paper artworks is therefore crucial. With its large specific surface area and strong adsorption capacity, nanocellulose effectively neutralises acidic substances in paper, prolonging its lifespan⁵⁰. The NanoForArt project, participated in by Baglioni et al. of Florence University, focuses on new nanomaterials and response systems for strengthening, cleaning and pH regulation of immovable works of art, and there are many studies on alkaline nanoparticles in deacidification⁵¹. Baglioni⁵² explored the non-aqueous phase deacidification system with $\text{Ca}(\text{OH})_2$ and $\text{Mg}(\text{OH})_2$ nanoparticles as the core. Nanoparticles were dispersed in non-aqueous media such as short-chain alcohol or cyclohexane to avoid direct damage to cellulose by free OH. Instead, mild and controlled acid neutralisation is achieved through the slow release of OH^- from free water originating from the environment, which reacts with the H^+ in the substrate in a neutralisation reaction; Nanoparticles that do not participate in neutralisation will further react with CO_2 in the air and convert to CaCO_3 or MgCO_3 , forming alkaline reserves inside the substrate. For the deacidification of cellulose-based cultural heritage, Poggi⁵³ prepared a stable $\text{Ca}(\text{OH})_2$ dispersion that does not require purification by using metallic calcium and short-chain alcohols as raw materials, first reacting to form an alkoxide intermediate, and then hydrolysing. Utilising cellulose adhesives and nanocellulose, alkaline particles are stably loaded with a high specific surface area and hydroxyl active sites to inhibit agglomeration. The carrier’s dispersing action ensures uniform distribution of alkaline substances across the paper, enabling neutralisation reactions with acidic components to elevate pH levels. Simultaneously, the carrier’s nanoscale pores or network structure delays alkaline substance release, forming a sustained alkaline reserve for prolonged deacidification. Neutralisation efficiency is optimised

through ion exchange or chemical bonding, as illustrated in Fig. 2. Certain carriers may concurrently enhance paper mechanical strength or impart superhydrophobic properties. Protective capabilities can be further extended by incorporating functional materials such as flame retardants or antimicrobial agents.

For instance, Ma⁵⁴ et al. employed chemical vapour deposition (CVD) to combine CNC with CaCO_3 particles. Following modification with polydimethylsiloxane (PDMS) and methyltrimethoxysilane (MTMS), the paper acquired superhydrophobic properties whilst achieving self-cleaning functionality, whereby water droplets could roll away surface contaminants. The incorporation of CaCO_3 also endowed the coating with acid-removing capabilities, raising the alkaline reserve of treated historical paper to 1.235 mol/kg. This approach has been successfully applied to the conservation of wheat straw pulp paper dating from 1954. Amornkitbamrung⁵⁵ et al. employed trimethylsilyl cellulose (TMSC) to deposit calcium carbonate (CaCO_3) and magnesium hydroxide ($\text{Mg}(\text{OH})_2$) nanoparticles—stabilised in hexamethyldisiloxane (HMDSO)—as deacidifying agents. Through an immersion coating process, these nanoparticles were deposited onto the surface and interior of artificially acidified filter paper and a 1913 historical paper. The alkaline nanoparticles reacted with acidic constituents within the paper via acid-base neutralisation, thereby neutralising acidic components, elevating the paper’s pH, and introducing alkaline reserves to achieve deacidification. The CaCO_3 /TMSC coating demonstrated superior performance to $\text{Mg}(\text{OH})_2$ /TMSC in enhancing paper tensile strength and folding durability. Li et al.⁵⁶ selected a composite of 0.3% bacterial cellulose (BC) and 1.0% ZnO nanoparticles for paper deacidification and consolidation. A spray coating method was applied to the BC/ ZnO suspension onto the surface of the 1980 Xinhua Daily newspaper, forming a thin film structure where ZnO particles were loaded within a BC three-dimensional network. Performance testing was conducted after drying. The untreated paper exhibited a pH of 5.87, which increased to 7.79 post-treatment and remained at 7.65 after ageing. Furthermore, zinc ions from the ZnO nanoparticles penetrated fungal cells via cell membranes, reacting with protein genes within the nucleus to disrupt cellular respiration and metabolism, thereby achieving a certain degree of antibacterial efficacy.

Fig. 3 | Schematic diagram of nanocellulose combined with a cationic polymer for antibacterial treatment of paper cultural heritage. This work is licensed under CC BY-NC-ND 4.0. This figure illustrates the process of nanocellulose cooperating with a cationic polymer to achieve antibacterial treatment for paper cultural heritage. The green fibrous structure represents nanocellulose, and the light blue dots stand for cationic polymer; their combination enables the dispersion of cationic polymer and inhibits its aggregation. The cationic polymer carries positive charges (described as “positive charges” in text), and it adsorbs to substances with negative charges (described as “negative charges” in text) through electrostatic interaction, thus acting on the yellow layered structure, which is the phospholipid bilayer. The phospholipid bilayer corresponds to the cell membrane of microorganisms; after the above interactions, the contents of mould cells (the pink oval structure) flow out, thereby achieving the antibacterial effect. In this figure, the symbols correspond to: green fibrous structure for nanocellulose, light blue dots for cationic polymer, yellow layered structure for phospholipid bilayer, and pink oval structure for mould cells.



Additionally, acid removal can be achieved through graft copolymerisation or chemically modified cellulose combined with alkaline particles. In the APACHE project, which aims to solve the long-term preservation problems of billions of objects collected in museums, libraries and archives. Xu⁵⁷ et al. employed a CDI-mediated method to graft oleic acid onto CNC surfaces, enhancing its dispersion in ethanol. Subsequent addition of alkaline nanoparticles strengthened interactions between grafted nanocellulose fibres, forming clustered structures that synergistically achieved acid removal and reinforcement.

In addition to loading alkaline particles onto cellulose derivatives, Zhang⁵⁸ et al. achieved uniform mineralisation on a BC nanofibre network by utilising alkaline phosphatase (ALP) to catalyse Ca GP decomposition into HAP and urease to catalyse urea decomposition into CaCO₃. Hydroxyapatite (HAP) and calcium carbonate (CaCO₃) mineralised BC membranes were prepared. Multiscale nanochannels enabled ion exchange between paper and the BC membrane (Ca²⁺ migrating to paper, H⁺ migrating to BC). Mineralised BC membranes achieve acid removal through direct contact with paper, eliminating the need for solution immersion and thereby avoiding fibre swelling or solvent toxicity issues. Furthermore, BC membranes can be removed without damage, satisfying the principles of reversibility and minimal intervention in cultural heritage restoration.

Antimicrobial

Most cellulose ethers are primarily employed in aqueous systems, where water promotes bacterial growth. Bacterial proliferation frequently accompanies mould formation. Moulds induce bond cleavage in adjacent unsubstituted dehydrated glucose units of cellulose ethers, reducing polymer molecular weight. Consequently, preservatives must be added to aqueous cellulose ether solutions for prolonged storage, even for antimicrobial variants¹⁶. Nanocellulose can generate antimicrobial agents by inhibiting microbial growth. In their research on the reversible deacidification and preventive protection of paper-based cultural heritage using mineralised BC membranes, they selected BC as an important category of nanocellulose, which features high purity, high crystallinity, and a three-dimensional nanofiber network structure (with a single fibre diameter of 30–80 nm). Its dense network can physically prevent the attachment and penetration of microorganisms, and its high specific surface area also creates conditions for the subsequent loading of antibacterial components^{58,59}.

Similarly, the natural nanocellulose itself has limited ability to inhibit bacteria, and in practice, it needs to be compounded with other materials to play the role of loading and dispersion of nanocellulose, in order to enhance the effect of bacterial inhibition⁶⁰. Ma et al.⁶¹ proposed a composite-enhanced anti-mould method based on CNC and polyhexamethylene guanidine (PHMG). As a cationic polymer, PHMG's positively charged molecular chains undergo electrostatic adsorption with negatively charged microbial cell membranes. This disrupts the integrity of the phospholipid bilayer, leading to leakage of cellular contents and cell death. This composite system exhibits significant inhibition against moulds such as *Aspergillus niger*. PHMG uniformly distributes across the fibre surface, forming a sustained antimicrobial barrier, while CNC fill the fibre pores to create a dense network. Fu⁶² et al. utilised CMC as a substrate, preparing diacetyl carboxymethyl cellulose (DCMC) via sodium periodate oxidation. This was then combined with trimethoprim lactate (TMP) and aminated berberine (BBR-NH₂) through a Schiff base reaction to synthesise the TMP-DCMC-BBR composite protective solution. The cationic structure of BBR binds to negatively charged components (phospholipids) on bacterial cell membranes, increasing membrane permeability and causing intracellular leakage. TMP acts as an antimicrobial synergist by inhibiting bacterial dihydrofolate reductase, blocking tetrahydrofolate synthesis and thereby suppressing nucleic acid and protein synthesis. CMC, a water-soluble cellulose derivative, utilises the carboxymethyl and hydroxyl groups on its molecular chains to uniformly disperse BBR and TMP through hydrogen bonding and electrostatic interactions. This prevents agglomeration of the two components, ensuring full exposure of the antimicrobial agents. The product demonstrates effective inhibition against *Escherichia coli* and *Staphylococcus aureus*. Furthermore, this protective solution fills interstitial spaces within paper fibres and enhances fibre bonding. PHMG, as a cationic guanidine polymer, BBR, as a natural herbal ingredient, and TMP, as an antimicrobial agent with high efficiency and low toxicity, are all safe and non-toxic, and meet the requirements of cultural heritage protection. Both approaches utilise nanocellulose to disperse cationic polymers, which disrupt fungal cell membranes through electrostatic adsorption, leading to intracellular fluid loss and cell death, as illustrated in Fig. 3.

All these approaches employ cellulose derivatives as a substrate, combined with other antimicrobial materials, achieving synergistic physical

reinforcement and chemical antimicrobial conservation for paper-based cultural artefacts.

Application in the conservation and restoration of wooden heritage

Consolidation

Currently, cellulose derivatives play an indispensable role in the conservation of wooden artefacts^{63–65}. Owing to their high compatibility with wood, cellulose derivatives are frequently employed in the treatment of diverse wooden artefacts. Cellulose ethers are utilised in art restoration due to their excellent ageing resistance and versatility across a range of organic and aqueous solvents⁶⁶. Nanocellulose has demonstrated multiple applications, such as reinforcing coatings for ancient timber, degraded wood, and waterlogged wood⁶⁷. Cipriani⁶⁸ and others pioneered the use of modified cellulose as a wood consolidation agent, preparing cross-linkable cellulose ethers including allyl cellulose, allyl carboxymethyl cellulose, and allyl N-hydroxypropyl cellulose to reinforce timber.

Waterlogged archaeological timber undergoes degradation from acids, alkalis, salts, and microbial activity during prolonged burial. This leads to severe degradation of components like cellulose and hemicellulose, causing the wood's cellular structure to gradually disintegrate and its mechanical strength to markedly diminish. Upon exposure to air, the fragile cell walls of waterlogged archaeological timber are prone to collapse due to capillary forces and the high surface tension of evaporating water. This ultimately causes wood shrinkage, deformation, and even cracking, rendering it irrecoverable and compromising the preservation of valuable historical information⁶⁹. Walsh⁷⁰ et al., in the conservation of the 16th-century British warship HMS Mary Rose, evaluated the suitability of polyethylene glycol (PEG) and its derivatives monomethyl ether and dimethyl ether, alongside chitosan, guar adhesives, and HEC, as consolidants for waterlogged wooden artefacts. HEC demonstrated superiority over conventional PEG materials in chemical stability, wood compatibility, and structural support properties when used as a water-soaked timber reinforcement agent, while also offering low toxicity and environmental benefits. Although its high viscosity may impede deep penetration, its excellent performance at low concentrations renders it a highly promising alternative material, particularly suited for preserving timber artefacts prone to acid degradation or exhibiting fragile physical structures. Kluge⁷¹ et al. investigated the reinforcement effects of CNF and CNC on independent coating films of water-based wood coatings. They found that CNF's high aspect ratio readily forms network structures, enhancing mechanical properties; whereas CNC's short rod-like structure has a weaker network-forming capability, enabling it to retain ductility while providing reinforcement. Unmodified CNC strikes a favourable balance between reinforcement efficiency, ductility, and transparency, making it an excellent reinforcing filler.

For non-waterlogged wooden artefacts, Younis⁷² et al. investigated the efficacy of CNF in reinforcing HPC for wood conservation. As a cellulose ether, HPC exhibits good wood compatibility and water solubility but suffers from low tensile strength and elastic modulus, rendering it inadequate for reinforcing severely damaged wooden artefacts. As a nanoscale reinforcing filler, CNF combined with HPC forms a network structure within the matrix, enhancing stress transfer efficiency. Its nanoscale dimensions ensure effective filling of wood pores. Post-treatment, the wood exhibits a stable chemical structure and minimal colour change, confirming that this material can effectively enhance mechanical properties while preserving the artefact's original appearance. The 30% CNF composite proves suitable for moderately damaged porous timber, offering both penetrative reinforcement and avoiding surface accumulation caused by high viscosity. Whilst the 50% CNF formulation exhibits increased viscosity compared to the 30% variant, its insufficient penetration depth renders it unsuitable for deep-level reinforcement.

For wooden artefacts affected by decay and microbial damage, Basile⁷³ has developed a CNC-based consolidant. This involves applying a CNC suspension, prepared via sulphuric acid hydrolysis, either alone or blended with lignin and PDMS, to decayed Norwegian spruce timber. Pure

CNC exhibits particle sizes of approximately 15–20 nm, a crystallinity index of 89%, and excellent stability in aqueous solutions. Its high specific surface area and hydroxyl-rich surface characteristics provide a structural basis for forming hydrogen bonds with wood fibres. Pure CNC treatment significantly enhances wood's storage modulus. While CNC-PDMS blends (CPL) exhibit lower storage modulus than pure CNC, they markedly improve wood hydrophobicity, achieving contact angles of 110°–130°. Furthermore, CNC exerts minimal influence on colour changes and surface roughness alterations in wood coatings under accelerated ageing conditions. Vardanyan⁷⁴ et al. observed that incorporating unmodified CNC into UV-curable water-based polyurethane acrylate transparent coatings significantly improved colour stability on wood substrates after accelerated ageing. ΔE in a 1200 h accelerated ageing test, the UV-cured wood varnish with 2% CNC showed superior colour stability with an overall ΔE of approximately 22.4. In contrast, the pure resin varnish without CNC showed a more significant change in colour after ageing, with a ΔE of approximately 28, while the addition did not compromise optical transparency or other properties, rendering it suitable for protecting ancient architectural timber components.

When holes and cracks appear in the wooden cultural heritage, and its structural stability, historical characteristics and aesthetic value are damaged, consider filling in the deficiencies, and MCC in combination with other fillers and binders can be very effective in filling in the deficiencies⁷⁵. Cataldi et al. showed that the addition of MCC can enhance the glass transition temperature and thermal degradation stability of the composite material, reduce the coefficient of thermal expansion, and at the same time, enhance the stiffness, fracture extensibility, fracture stress, and creep stability of the material, which is suitable for outdoor wood artefacts. MCC has a higher hygroscopicity than pulp due to its higher degree of crystallinity, and has a higher resistance to water swelling, which makes it suitable for outdoor environments where there are large fluctuations in moisture content^{76–78}. However, Fulcher's results showed that pulp compounded with HPC also fills wood artefact fissures well⁷⁹.

These studies collectively demonstrate that natural nanocellulose-based materials offer advantages such as enhanced mechanical properties in cultural heritage conservation and restoration. While differing in material types, application scenarios, and performance optimisation focuses, they collectively provide crucial insights for developing environmentally friendly and efficient conservation and restoration materials.

Adhesion

Cellulose derivatives are frequently modified for application in wood adhesives. Physical modification involves directly incorporating nanocellulose into adhesive matrices such as urea-formaldehyde resins or polyvinyl acetate; chemical cross-linking employs agents like glutaraldehyde or borax to establish chemical bonds between nanocellulose and the adhesive matrix, forming a network structure that enhances composite material properties⁸⁰. In the restoration of wooden artefacts, selecting an appropriate adhesive constitutes another critical aspect of preserving wooden artworks, as incorrect adhesives may inflict irreversible aesthetic and mechanical damage⁸¹. Cellulose derivatives can replace traditional formaldehyde-based adhesives, reducing formaldehyde emissions from wood composites and aligning with conservation principles. Furthermore, nanocellulose can function both as an adhesive and a structural reinforcer within various adhesive systems^{82,83} while also enhancing other adhesives⁸⁴, thereby promoting environmentally friendly and low-toxicity formulations consistent with conservation principles. Liu⁸⁵ employed 3-aminopropyltriethoxysilane (APTES) modification to form an amino-rich functional layer on wood surfaces. Grafting MCC onto APTES, to produce amine-functionalised cellulose (AC). Cross-linking this with the branched epoxy compound EAGE4 yielded a cellulose-based adhesive exhibiting superior water resistance compared to most bio-based adhesives, offering a novel direction for designing high-performance, environmentally friendly wood adhesives. Podlena⁸⁶ et al. investigated the regulatory effects of polyethylene oxide (PEO), HPMC, CNF, PVA, and lignin on the properties of soy protein-based wood

adhesives. CNF was found to act as a nanoscale reinforcing phase, enhancing adhesive cohesion, while the synergistic combination of CNF and lignin effectively improved the bonding strength of soy protein adhesives. Results indicate that SPI (soy protein isolate)-CNF-L (lignin-containing) at 9% solids content demonstrated optimal performance on southern yellow pine, significantly surpassing commercial urea-formaldehyde (UF) adhesives while exhibiting zero formaldehyde emissions. Kaboorani⁸⁷ et al. investigated the enhancement of CNC on PVA wood-based adhesive properties. CNC significantly increased PVA's bonding strength. Microstructural analysis revealed CNC forming a network within PVA as 150–250 nm rod-like structures, improving PVA's mechanical properties and thermal stability through nano-reinforcement and network-building mechanisms. However, unmodified hydrophilic CNC agglomerates at concentrations of 2% and 3%, proved difficult to disperse within PVA and thus limited improvements in bonding performance.

Applications in the conservation and restoration of oil paintings and textile heritage

Consolidation

Traditional oil painting canvases exhibit a multi-layered structure comprising the canvas substrate, adhesive layer, painting medium, pigment layer, and varnish composed of natural or synthetic resin mixtures⁸⁸. Natural fibre canvases such as linen and cotton degrade due to temperature and humidity fluctuations, acidic environments, and other factors, leading to diminished mechanical properties. This degradation subsequently causes pigment layer cracking and canvas tearing⁸⁹. Traditional canvas reinforcement methods, such as lining, suffer from issues including poor reversibility, material toxicity, and alteration of canvas properties, while natural adhesives readily cause canvas shrinkage. Cataldi⁹⁰ et al. systematically compared the performance differences between CMC and CNC-filled Aquazol adhesives. The latter, balancing mechanical properties with optical transparency, is suitable for canvas reinforcement.

Nanocellulose, possessing high strength, transparency, lightness, biocompatibility, and renewability, can be employed for oil painting canvas reinforcement⁹¹. In the NanoRestArt project, which aims to develop and apply nanotechnology to solve technical problems in cultural heritage conservation and improve the quality of restoration and long-term preservation of cultural heritage, there are many achievements discussing the use of nanocellulose to strengthen oil canvases^{91,92}. CNF, carboxymethylated cellulose nanofibrils (C-CNF) and CNC are used to reinforce oil painting canvas. Bridarolli explored the feasibility of CNF and CNC for canvas reinforcement because of the stress caused by the difference in mechanical behaviour of each layer of painting due to the change of relative humidity (RH). CNF and CNC were applied by the blade coating method and characterised by experiments. The results showed that two kinds of nanocellulose formed a continuous deposition layer on the canvas surface, and the initial colour change was small ($\Delta E < 1$). The stiffness of the canvas increased after treatment. CNC treatment was better than CNF treatment because of higher mass coverage, stiffness stability under mechanical enhancement and RH change and $\Delta E < 3$ after accelerated ageing. It was confirmed that nanocellulose had the potential for canvas reinforcement, and CNC performance was better⁹³. Kolman⁹⁴ developed a method combining polyelectrolyte-treated silica nanoparticles (SNPs) and CNF to consolidate canvas. CNF is easy to interweave on the canvas surface after spraying to form a continuous film, reducing surface cracks and improving canvas ductility; SNP is modified by cationic polyethyleneimine PEI and anionic CMC to form CMC@SNP, which is negatively charged by CMC in the outer layer, which can avoid flocculation with CNF, which is also negatively charged. Meanwhile, it can penetrate into the interior by capillary action of the canvas fibre network, forming support at the single fibre scale to enhance canvas stiffness and balance stiffness and ductility.

BNC is also used for textile reinforcement. Aiming at the problem that historical silk fabrics are easily degraded by environmental factors and irreversible damage exists in traditional synthetic polymer reinforcing agents, Wu et al.⁹⁵ prepared artificially aged silk samples (AAS) with

mechanical properties close to those of excavated historical silk fabrics through UV-ozone ageing, and used *Bacillus xylosus* fermentation to prepare BNC and complete the reinforcement through the spraying-culture process. The tensile strength of AAS was increased from 40 N/m to 125 N/m, and the onset temperature of thermal degradation was increased from 252 °C to 281 °C. The colour difference of the reinforced samples was less than 1.00. After 12–24 h of UV-ozone ageing, BNC can be degraded gradually without damaging the original structure of the silk fibre. The mechanical properties and crystallinity of the silk samples fell back to the initial level with the degradation of BNC, which proved that the BNC has both excellent reinforcing efficiency and controlled degradation.

Cellulose ethers such as HPC were selected by the British Museum as an adhesive for restoring an ethnic costume due to their ability to form a lightweight, uniform, transparent and non-reflective film; CMC was employed to bond detached metal strips on a 17th-century Venetian Doge's hat from the Ashmolean Museum in Oxford⁹⁶. In the study of Böhme et al.⁹⁷, HEMC was used as a matrix with nanocrystalline cellulose (NCC) to form a rigid network, and the high specific surface area of NCC was used to enhance interfacial bonding between fibres and improve mechanical strength. The non-polar system was modified by silanization to achieve the solubility of the material in non-polar solvents and avoid interaction with the oily painting layer. The water-soluble HEMC of the polar system can be removed by aqueous warming, and the silanized layer of the non-polar system can be stripped off by mild solvents. Markevicius⁹⁸ has conducted research on the reinforcement of sensitive artworks containing fragile, porous, powdery media, and has used Ultra-Low Viscosity Hydroxypropyl Methylcellulose (ULV-HPMC) with Ultrasonic Atomization for the non-contact reinforcement of fragile, porous, powdery oil paintings. Successful applications include Edvard Munch's *Alma Mater* painting at the Munch Museum and a 19th-century Thai gum watercolour at the Victoria and Albert Museum. Both of them focus on low viscosity and low risk applications of cellulose ether materials. The former focuses on cellulose ether modification and nano-composites to solve the problem of acid removal and reinforcement of the canvas support layer, while the latter focuses on the ultrasonic atomization and non-contact reinforcement of ultra-low-viscosity HPMC to solve the problem of liquid sensitivity of powdered paintings, which together perfect the application of cellulose ether in art protection.

Due to photochemical reactions and other reasons, the pigment layer of oil paintings and cultural heritage suffers from degradation and peeling off⁹⁹. In Oporan et al.'s study, the results of characterization experiments comparing a group with CNF applied, a group with CNF applied to the back of the canvas, and an untreated control group after 54 h of exposure to direct sunlight revealed that 4.5% CNF applied to the pigment layer of the paintings had a good consolidation effect and could effectively slow down the degradation of the pigments caused by sunlight exposure¹⁰⁰.

Cleaning

Removing varnish layers constitutes a critical step in artefact cleaning during oil painting restoration, demanding uniform treatment, residue-free removal, and minimal damage to the painting layer¹⁰¹. As renewable nanomaterials, CNF and CNF exhibit surface chemistry and morphology controllable via TEMPO oxidation. Microemulsion, gel and other colloidal systems can achieve low toxicity, high selectivity and controllable cleaning goals through nanostructure regulation, solve the residual, penetration and toxicity problems of traditional solvent cleaning, and verify in the conservation of murals, oil paintings, cultural heritage and other cultural heritages^{102–104}. Caruso¹⁰⁵ et al. utilised CNC as a stabiliser to prepare water-in-oil Pickering emulsions for removing natural resin varnish from canvas oil paintings. They further explored the use of the green solvent ethyl acetate as an alternative to conventional petroleum-based solvents, enabling the emulsion to efficiently remove varnish without damaging the painting layer. Laserna¹⁰⁶ prepared nanofibre cellulose aerogels from glycerol-crosslinked diacetyl cellulose. These aerogels exhibited high water absorption capacity,

surface adaptability, and reusability. Loaded in green solvents, they effectively removed natural resin varnish from canvas.

Deacidification

Textile artefacts such as canvas, cotton and linen fabrics, silk fabrics, etc., face the problem of susceptibility to acid-catalysed hydrolysis. Sources of acid include the ageing and decomposition of the raw materials themselves, the erosion of environmental pollutants, and acidic residues in auxiliary materials such as dyes or adhesives, which ultimately lead to a decrease in the degree of polymerisation of the fibres, a decline in their mechanical strength, and their brittleness or even fracture. As a key preventive measure for textile heritage conservation, the core objective of acid removal is to neutralise the inherent acidity and deposit alkaline reserves to block the acid-catalysed degradation chain, while meeting the principle of “minimal intervention” to avoid secondary damage to the fibre structure, pigments or original auxiliary materials¹⁰⁷.

The rise of nanotechnology provides an efficient solution for deacidification of textile artefacts, achieving a balance between acid neutralisation and fibre compatibility by virtue of nanoparticles' high specific surface area, good permeability and dispersibility. Currently, the mainstream nano acid removal materials include CaCO_3 , $\text{Ca}(\text{OH})_2$, MgO and other alkaline nanoparticles^{108,109}. In order to further optimise the performance, the researchers will be using a nanocellulose and alkaline materials composite. Nanocellulose can not only optimise the application of alkaline deacidifier performance and stability of the action, but also can be reinforced on the heritage, improving the mechanical properties of the heritage. Palladino et al.¹¹⁰ compared the effects of the combination of silica nanoparticles, SNP and CNF/CNC for reinforcement, CMC@ CaCO_3 for deacidification, and the combination of deacidification followed by reinforcement for the deacidification of iron-tanned dyed cotton. Through the characterisation, it was found that only the reinforcement treatment could slightly improve the low deformation modulus of elasticity, but it could not effectively neutralise the acidity, and the mechanical properties decreased sharply after accelerated ageing. In contrast, the combined treatment group could increase the pH steadily to 7.0–7.5, maintain the neutral alkaline range after ageing, and increase the mechanical properties, and the nanocellulose residue decreased by 40% after ethanol wiping, which increased the reversibility. In addition, the colour of the co-treated samples was slightly deeper, which partially alleviated the reddish and yellowish colouration caused by the decomposition of the iron-tanned dyes, but only for dark iron-tanned dyed cotton. Compounding nanocellulose with alkaline particles can also be used directly for deacidification and reinforcement. For example, Wei et al.¹¹¹ developed an aqueous suspension of CNF and MgO for the reinforcement and deacidification of a Ming Dynasty genealogical scroll painting made of textile cotton, with CNF enhancing the structural stability by strengthening the bonding force between fibres, and nano- MgO forming a long-lasting alkaline reserve to inhibit acid-catalysed hydrolysis. The 0.6% CNF–0.15% MgO nanosuspension was applied to the restoration of the real scroll painting, and the pH of the painting was increased to 7.2 after the restoration. The mechanical properties of the painting were improved with the light transmittance of >85% and the colour difference of $\Delta E < 2$ with little visual impact.

Prospects and challenges for cellulose derivatives in cultural heritage conservation

VOC emissions from cellulose ethers

Whilst cellulose ethers find extensive application in cultural heritage conservation, certain variants exhibit issues including volatile organic compound (VOC) emissions, material stability concerns, and application limitations. In the APACHE project, it is an important goal to develop a new generation of active intelligent storage boxes, filing boxes and display cabinets, improve storage and display to solve the problem of cultural heritage preservation, and also focus on solving the problem of VOC release during cultural heritage storage. The “Novel Archive Box” in the project results contains a composite system composed of nanocellulose, colloidal

silica and polyethyleneimine as a VOCs adsorbent. Relying on the synergistic effect of the high specific surface area of nanomaterials and the abundant functional groups of PVA, it can efficiently capture harmful gases such as NO^+ and reduce the corrosion risk of VOCs on cultural heritage^{112,113}. The Oddy test, introduced by Dr Andrew Oddy at the British Museum in the 1970s, is an accelerated corrosion test designed to identify materials potentially emitting volatile substances harmful to museum artefacts. The method involves placing material samples in test tubes under conditions of 100% RH and 60 °C for 28 days, with three metal test pieces (copper, silver, and lead) inserted into the tube's silica gel stopper. At the conclusion of the test, the degree of corrosion on each test piece is assessed¹¹⁴. Steger³⁰ et al. employed the Oddy test to evaluate commercially available cellulose ethers, providing theoretical justification for their potential use in cultural heritage conservation and restoration. Industrial-grade HPCs, such as Klucel G, release high concentrations of acetic acid, with corrosion products including cuprite, manganese oxide, white lead, and lead formate, indicating the presence of corrosive VOCs like formic acid. However, the corrosion issues with HPC stem not from the material itself but from residual impurities introduced during production. Thus, enhancing HPC purity would mitigate this problem. The study also tested small quantities of HEC, EC, and MC, though most failed the tests. HEC and EC primarily released acetic acid due to residual acetate salts, while some MC samples emitted VOCs like formic acid from residual impurities. Additionally, MHEC and MHPC demonstrated overall good stability, with failures primarily attributed to historical samples or specific formulations containing residual impurities (acetate, formic acid, sulphates). CMC exhibited stable performance, with only minor corrosion observed in some older samples due to trace impurities.

Overall, MC, CMC, MHEC, and MHPC demonstrated the best performance, achieving the highest pass rates in the Oddy test. Results indicate that refining production processes—such as enhancing purity and controlling residual impurities—is crucial for ensuring Oddy test compliance. Furthermore, the safety of cellulose ethers within the same category is significantly influenced by production methods, purity levels, and batch variations. Their suitability for cultural heritage conservation must therefore be assessed based on specific product information.

Difficulties in hydrophobic modification of nanocellulose

When nanocellulose serves as a reinforcing agent, selecting hydrophobic polymers such as polylactic acid (PLA), polyethylene (PE), and polypropylene (PP) as the matrix material reduces its aspect ratio. Owing to nanocellulose's inherent hydrophilicity and lack of reactive functional groups compatible with hydrophobic matrices, incompatibility arises. This leads to self-agglomeration via intermolecular hydrogen bonding¹¹⁵, hindering uniform dispersion within hydrophobic matrices. This incompatibility not only diminishes the aspect ratio of nanocellulose, thereby weakening its reinforcing effect, but may also induce phase separation and voids within the composite material, adversely affecting stress transfer and thermal stability. Although surface modification can partially reduce surface energy and enhance compatibility with hydrophobic matrices, the modification process is often complex and costly. For instance, solvent replacement methods involve cumbersome operations, while supercritical drying technology faces challenges in industrial implementation. Furthermore, modified nanocellulose may face issues such as crystalline structure disruption and diminished thermal stability, while unmodified nanocellulose struggles to act as a nucleation agent within hydrophobic matrices, further limiting its application potential in hydrophobic polymer-matrix composites¹¹⁶.

Nanocellulose agglomeration

Increasing the loading of nanocellulose may diminish material properties. Good dispersibility is crucial for nanocellulose to effectively enhance polymers, yet excessive amounts often induce entanglement or even agglomeration, hindering uniform dispersion within the matrix¹¹⁷. Such agglomeration induced by high loading diminishes composite performance due to the highly heterogeneous two-phase interface between cellulose

aggregates and the matrix, thereby limiting the extent to which cellulose fillers enhance reinforcement. This phenomenon is more pronounced in hydrophobic polymers: owing to their high interfacial polarisation, the optimal loading of nanocellulose in hydrophobic polymers is markedly lower, and nanocellulose within these polymers tends to reach supersaturation prematurely¹¹⁸. Although surface modifications (such as introducing charges or hydrophobic layers) can partially suppress agglomeration, these processes are often complex and may compromise the crystalline structure and intrinsic properties of nanocellulose. Consequently, achieving its efficient dispersion remains a critical issue requiring urgent resolution.

CNC films exhibit low strain

In addition to enhancing the rigidity of the fibres of cellulose-based artefacts, increasing fibre flexibility is one of the indicators that should be considered for the restoration of artefacts. CNC films are prone to brittle fracture at low strains. In Nechyporchuk et al.⁹¹'s study on the application of nanocellulose for canvas consolidation, CNC exhibited specific advantages, yet its limitation of brittle fracture remained prominent. From a mechanical perspective, CNC features a significantly lower aspect ratio compared to CNF due to its short rod-like structure. This structural characteristic not only reduces the elongation at break of the canvas post-coating but also renders it susceptible to brittle fracture in the low-strain region. Although the stiffness of canvas coated with three layers of CNC can match that of a freshly painted canvas within this region, effectively supporting the pigment layer, the reduced elongation at break indicates poor adaptability to the ambient temperature and humidity conditions of the canvas. Furthermore, it struggles to accommodate the dynamic deformation of the canvas induced by temperature and humidity fluctuations or minor external forces. In addition, while the low reinforcement efficiency per unit weight can be mitigated by increasing the CNC suspension concentration (3.00 wt%) and the number of coating layers, the inadequate deformation adaptability stemming from its inherent brittleness has not been resolved.

It has been pointed out that SRSF-CNC composite system can improve the flexibility of aged silk. CNC can avoid the formation of brittle β -folded crystal membrane by single high concentration of SRSF (silk protein), and induce the generation of more α -helical crystalline structure of SRSF through hydrogen bonding and electrostatic action in low SRSF concentration, reduce the proportion of random curling, so as to make composite membrane retain the movement space of molecular chain while maintaining the structural stability; meanwhile, the high mechanical strength of CNC synergizes with the flexible property of SRSF to avoid the brittle fibre caused by stress concentration. At the same time, the high mechanical strength of CNC and the flexibility of SRSF form a synergy to avoid the brittle fibre breakage caused by stress concentration. Experiments show that, after 1.35%/1.35% composite system treatment, the elongation at break of the three ageing types of silk are close to or completely restored to the original level, while a single SRSF or CNC treatment group can not achieve the same effect due to the loose structure or rigidity being too strong. However, the current research on other types of cultural heritage is less. The subsequent need to take into account the reinforcing effect and dynamic mechanical compatibility of the canvas protection research provides a direction¹¹⁹.

Conclusion

This paper systematically elucidates the current applications and technical pathways of cellulose derivatives in cultural heritage conservation. Owing to their structural characteristics, cellulose adhesives and nanocellulose demonstrate remarkable efficacy in mechanically reinforcing paper artefacts, deacidifying and ageing-retarding, consolidating and adhering wooden artefacts, and providing coating conservation for oil paintings and textiles. Their mechanisms of action encompass hydrogen bond network formation, nanoscale pore filling, and controlled release of alkaline substances. Despite challenges such as controlling nanomaterial dispersion, their renewable and low-toxicity properties align with the green

requirements of heritage conservation. Cellulose derivatives also hold significant potential for ceramic artefact conservation. While current research predominantly focuses on paper and wood, their mild nature, tunable rheological properties, and excellent film-forming capabilities make them promising candidates for the reinforcement and restoration of pottery, porcelain, and mural paintings^{120–124}. For fragile pottery, the adhesive properties of cellulose adhesives combined with the reinforcing effect of nanocellulose may enable precise fracture repair and structural reinforcement. For mural conservation, breathable, weather-resistant nanocellulose-based reinforcing coatings could be developed. These approaches hold promise for enhancing the precision and sustainability of cultural heritage conservation.

Current research provides theoretical underpinnings and case references for the practical application of cellulose derivatives in heritage conservation and restoration. Future efforts should focus on optimising composite material processes and expanding functional modification approaches to advance the deep application and technological innovation of these materials within the heritage conservation field.

Data availability

Date sharing is not applicable to this article as no dates were generated or analysed during the current study.

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Conceptualisation: Y.L., J.L., and S.W. Methodology: Y.L. and J.L. Validation: Y.L. and J.L. Formal analysis: Y.L. and J.L. Investigation: Y.L. Resources: S.W. Writing original draft preparation: Y.L. Writing—review and editing: S.W. Supervision: S.W. Funding acquisition: L.L. All authors have read and agreed to the published version of the manuscript.

Competing interest

The authors declare no competing interests.

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