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Review

A review on biopolymer-based treatments for consolidation and surface protection of cultural heritage materials

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ABSTRACT

Nowadays, the scientific community emphasizes the use of reversible and non-toxic materials in the field of cultural heritage. Biopolymers are one of the alternative materials to synthetic polymers and solvents that are dangerous for human health and for the environment, applied in consolidation and coating treatment. Natural biopolymers may be divided into polysaccharide, protein, and polyester: All of them are low cost, eco-friendly, and biocompatible, besides many physicochemical characteristics such as being transparent, soluble in water, hydrogel, and film-forming, and can be easily functionalized. The addition of nanoclay, essential oil, and active molecules improves the physicochemical properties of biopolymers and proposes smart response abilities to the new composite material. This work is intended to provide an overview of the development of biopolymers by considering the most general aspects and scanning the diverse substrates of application for the conservation and protection of cultural heritage.

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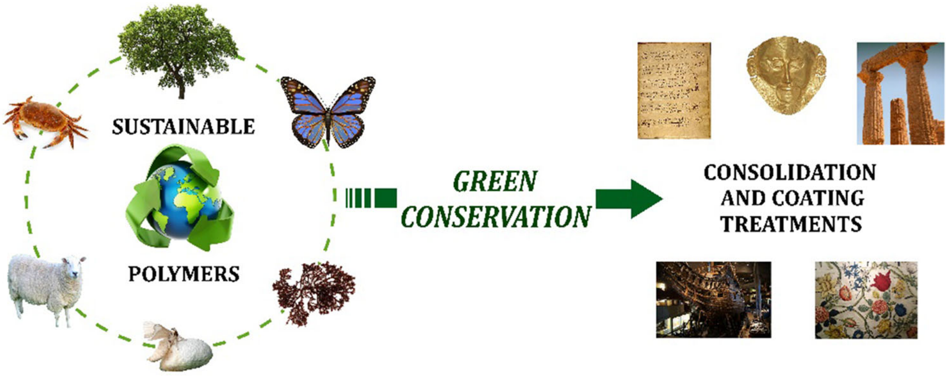
GRAPHICAL ABSTRACT



Introduction

Biopolymers and their derivatives have generated significant interest in the scientific community due to their distinctive features, such as being biodegradable, biocompatible, renewable, and having a high tensile strength. Just like other polymers, they consist of monomeric units bonded in long chains forming large molecules [1]. They are mostly derived from bio-sources including plant biomass, microorganisms, and agro-wastes. Biopolymers consist of nucleotides, proteins, polysaccharides, and fats. Since they are naturally derived from ecosystem, their economic value rises due to their biodegradability [2].

They can be divided into two main categories (natural and synthetic biopolymers) according to their origin. Polysaccharides and proteins are three types of natural biopolymers. Several sources such as animals, plants, or microorganisms are feedstock for natural biopolymers production, mostly consisting of carbohydrates and proteins. Chitosan, cellulose, lignin, starch, and pectin are some carbohydrate biopolymers; gelatin, collagen, fibroin, and keratin are examples of protein-based biopolymers [3, 4]. Bio-based polyesters, polyhydroxyalkanoates polylactide and polyamides are currently the most promising biopolymers derived by renewable resources [5]. It should be noted that bio-based polyesters can be obtained from natural sources, such as oils and fats, and they can be classified as aliphatic, aromatic monomers and elastomers [6]. Synthetic biopolymers are obtained through biological and/or chemical modification of the natural ones. They can be directly synthesized from fossil fuels or obtained from biomass through chemical processes or fermentation. Biopolymer segregation based on composition is present in laminates, composites, and blends. While synthetic biopolymers have a defined composition as part of their properties, as well as their chemical structures, natural biopolymers are less defined, but inherently bioactive because of the presence of natural extracellular matrix patterns [3, 7, 8].

Biopolymers are generating interest in a wide range of research areas of material science, but they are usually combined with other components (nanoparticles, polysaccharides, plasticizers) to improve their performances. Furthermore, by changing their physicochemical properties, such as linkage types, solubility, chain length, viscosity, or gelling potential, different materials with diverse applications could be obtained. Indeed, biopolymers-based materials aggregated in different ways such as sponges, films, and hydrogels have been developed [4].

The biocompatible and biodegradable properties, as well as their low toxicity, give to biopolymer-based materials a huge versatility, which allows them to be used in several fields (Fig. 1): They are becoming increasingly important in numerous sectors such as agriculture, food, medicine, pharmaceuticals, being applied as edible films, packaging materials,

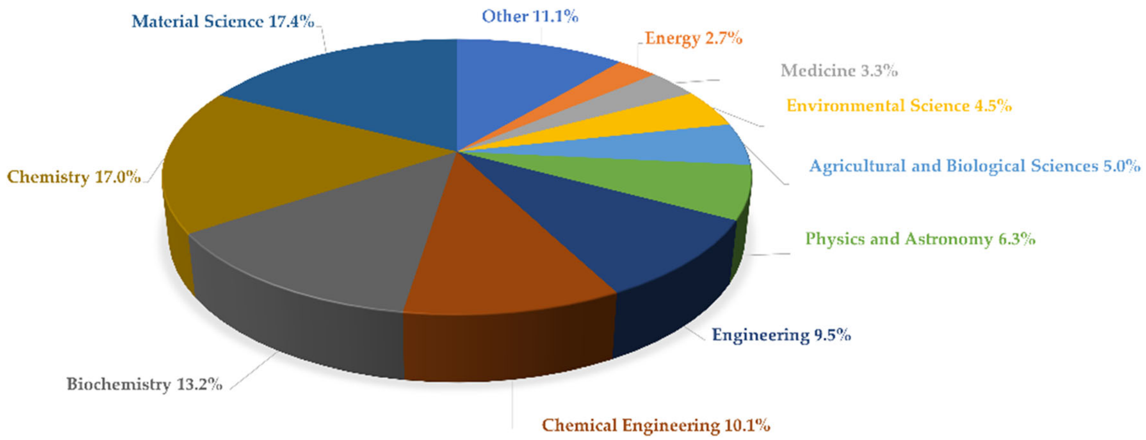


Figure 1 Biopolymers distribution in different subject categories. Data are from Scopus and they were obtained using as searching string TITLE-ABS-KEY ("biopolymer").

emulsions, and drug delivery materials. They also find important applications in the conservation of cultural heritage as green alternatives to the use of chemical products which expose to risk both environment and human health. Moreover, taking advantage of biopolymers, which are abundant and require a low-cost production process, may be a smart strategy at the outset to mitigate cost problems.

Biopolymers used in the conservation of cultural heritage

In recent years, the development of sustainable materials has been registered to reduce the environmental impact. In this context, a green approach is gaining ground in the cultural heritage research area and both restorers and scientists working in this field attempt to come up with innovative conservation materials taking into account environmental sustainability [9]. Therefore, for this purpose, biopolymers and their derivatives have found several applications in the cultural heritage field (Fig. 2) [10].

Artifacts are subjected to weathering over years, deteriorating because of physical, chemical, and biological factors usually working simultaneously. This may lead conservators to the strengthening of deteriorated materials (consolidation), removal of pollutant deposition layers or other unwanted surfaces (cleaning), and protection of substrates by long-lasting coatings (final protection). All these conservation procedures require the use of products that are compatible with the artifacts' original materials [11].

Concerning consolidation processes, the aim is to give back to the surface the lost compactness and adhesion between preparation and pictorial layers, preventing material losses by increasing their mechanical properties. The chosen products should be as much compatible as possible to the original binders in order to not change materials breathability and colors. They also must have a good durability and the capacity to penetrate the artefact substrate [12] Consolidation materials developed in the past or, indeed, still in use are several adhesives such as protein glues, gelatin, acrylic resins, waxes, polyvinyl alcohol, and emulsions, all materials which are often attacked by microbiological organisms [13, 14].

Regarding cleaning processes, aged varnishes, repaints, and dust are removed from easel or mural paintings to enhance artworks' readability because they can cause irreversible alterations harmful to conservation. Standard cleaning processes involve several organic solvents—such as ligroin, acetone, and ethanol—both in solution or gel systems, to remove varnish; emulsions or surfactants aqueous solutions for dirt removal; mechanical/physical methods such as scalpel to scrape off darkened areas. Sometimes the solvents used are harmful to both environment and operator, especially when the work is led in a small and with not air-conditioning room; moreover, the mechanical cleaning is not well controlled and gradual, leading to the removal of original substrates. The cleaning process must be controlled at every phase, selective and gradual, in order to maintain the original layers. Moreover, it should not produce any physical changes, such as abrasions or microfractures that can increase porosity

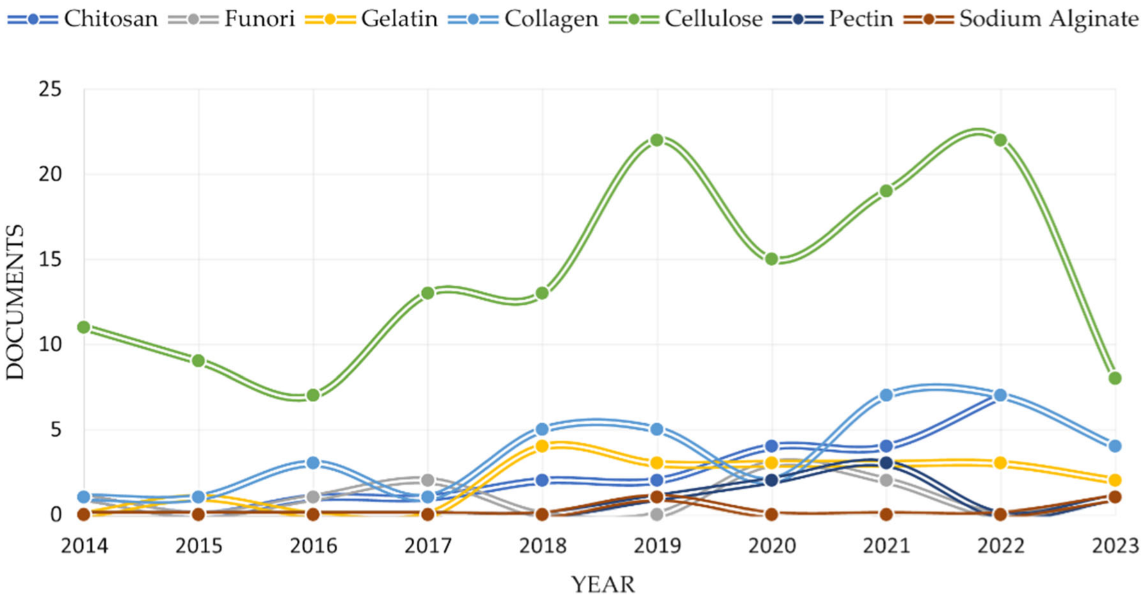


Figure 2 Data are from Scopus and they were obtained using as searching string TITLE-ABS-KEY (“biopolymer name” AND “cultural heritage”) or TITLE-ABS-KEY (“biopolymer name” AND “conservation” AND “artifacts”).

accelerating deterioration processes. Concerning protection procedures, they are applied because the water absorption by the facade of porous substrates is one of the main causes of physical, chemical, and biological material degradations. For this reason, it is important to use products which form a surface film permeable to steam, otherwise the process would lead to condensation on consequent detachments of some surface layers [12, 15].

Despite the usage of the conventional materials, traditional conservation procedures are replaced by more eco-friendly ones, which can also be chemically functionalized enhancing their mechanical properties but also giving them new features by adding specific products, which include antioxidants, antimicrobial, and hydrophobing agents [16–19]. This search for methods that are both highly selective and safe for operators and the environment, at the same time maintaining the effectiveness of the procedures has led to the development of the application of biopolymers in the cultural heritage field.

The current review will focus on the potential of biopolymer-based materials applied for the conservation of cultural heritage, specifically investigating consolidation products and protective coatings for different heritage substrates. Future research needs and perspectives are also highlighted along.

Protein-based biopolymers for consolidation treatment and protective coating

Gelatin

Gelatin is a hydrocolloid mainly composed of proline and glycine with a notable quantity of hydroxyproline, also containing small amounts of aromatic amino acids phenylalanine and tyrosine. It is made up of a diverse combination of high average molecular mass proteins, which are water-soluble, and able to form thermo-reversible films [20, 21]. Gelatin is used as a restoration material because of its gel and film forming. Perhaps the larger range of its properties was tested in the photographic emulsions field. Conservators have been increasing their interest in replacing synthetic polymers with more sustainable materials, leading to a gradual rise in the use of gelatin (derived from fish and mammals) as adhesive and consolidant in painting conservation treatments in recent years, especially in the field of filling modifications for canvas [22].

Gelatin properties, such as gel strength, water vapor permeability, and mechanical performance of films, UV barrier action, can be enhanced by mixing it with additional materials. It has been tested in combination with several plasticizers. The microstructure of gelatin, composed of tridimensional frameworks with microcrystalline linking points through molecules, causes higher brittleness upon system dehydration decreasing the possibility to consolidate gelatin when used in conservation treatments. This issue has been resolved by adding mono-, di-, olyols, and oligosaccharides to the biopolymer. The combination with these plasticizers granted gelatin-based consolidants a higher workability, flexibility, and extensibility, also reducing the risk of contraction [23]. In the last years, also the influence of antibacterial materials on gelatin-based adhesives and glycerol as plasticizers was tested. In particular, the impact of citronella oil was examined regarding gelatin mechanical properties, water vapor barrier characteristics, and other functional attributes. The gelatin film formation process, as well as the structure and final properties, was found to be affected by the combination of citronella oil and glycerol, according to both microscopic and spectroscopic investigations. These results underlined glycerol plasticizer effectiveness with gelatin-based adhesives, also indicating that citronella oil, beyond its biocide activity, enhances the adhesive mechanical properties when used in combination with glycerol [24].

Fibroin

Silk fibroin is a natural proteinaceous biopolymer primarily derived from silkworm (*Bombyx mori*) cocoons, and spiders (*Nephila clavipes*) as well. This robust and long protein fiber has been used by humans for over 3000 years to manufacture fine clothes and threads. The silk gland of the caterpillar synthesizes fibroin as two polypeptide chains connected by a disulfide bridge. The wider heavy chain is full of glycine and its structure is mostly formed by a repetition of Gly-Ala/Ser dipeptides [25]. Its structure is known to diffract X-rays, with a diffraction pattern distinctive of a folded β-sheet. This helped Pauling and Corey with the definition of this kind of structure [26].

Its advantageous characteristics, such as low toxicity, good mechanical properties, biocompatibility, and variable degradability, led to the application of silk fibroin as a promising biomaterial for biomedical and biotechnological fields [27, 28].

Recent works have also demonstrated its possible application in the conservation of cultural heritage as a consolidation agent for silk artifacts, due to its capability to form films with different structures. Specifically, it studied the possibility to change the mechanical behavior of films by modifying their internal structures. There is a chance to adjust the crystallinity parameter of films, altering the amount of fibroin contained inside the dispersions. (The more concentrated is the dispersion, the more crystallinity is achieved in the films.) It has been seen that the application of silk fibroin dispersions to aged silk fibers, forms between them several domains with different order degrees, influencing the mechanical properties. The application of concentrated dispersions of silk fibroin, enhanced in crystallinity, decreases the elongation length of aged silk fibers. Instead, by lowing silk fibroin concentrations, the dispersion increased in amorphousness improving the mechanical properties of fibers. As now could be easily predictable, the best results were given by the treatments with the dispersions having the lowest fibroin concentrations. Indeed, the treated fibers showed comparable values of tensile strength to pristine silk, and larger elongation [29].

Once demonstrated that silk fibroin could be used to consolidate silk artifacts, several adaptations of the treatment have been tested. Pretreating samples with transglutaminase (TG) and sodium caseinate (SC) and then spraying silk fibroin solution, an enhanced consolidation of fibers is recorded. Referring to the untreated fabric, the breaking stress and strain of the consolidated silk tissue are, respectively, increased by 20.89% and 27.15% [30].

Silk fibroin solution has been also tested together with nanocellulose, to find a procedure to consolidate historical silk items avoiding high fibroin concentrations. The presence of cellulose nanoparticles inside the dispersions accelerates the assemblage of fibroin, as proved by DLS measurement, besides the production of more compact aggregates. Treatments with these hybrid dispersions led to high improvements, outperforming the single component dispersion at the same concentration [31].

Collagen

Collagen is a widely found animal structural protein. Its structure consists of a three-strand rope, made of three polypeptide chains that coil around each other, where each chain twists individually in the opposite direction. This structure is composed of three essential amino acids—proline, glycine, and hydroxyproline—and each of them contributes to the specific function of collagen. Hydrogen bonds, as well as covalent bonds, keep strands held together binding adjacent NH and CO groups [32]. The main application of collagen is in the medical field, especially as a bone-filling material or drug deliverer. It can also be frequently found in the cultural heritage field but as a constituent material, not as a conservation one. Only in recent years, it has been applied by restorers for leather preservation. Conserving leather artifacts that are exhausted, torn, pulverized, or feeble, poses a considerable challenge for conservators. Such forms of deterioration are caused by aging, usage, and handling of artifacts, especially with books, as well as the materials employed in the manufacture of leather or finishing protection treatments. Since 1970, hydroxypropyl cellulose (HPC) has been commonly used for leather consolidation. More recently, a blend of acrylic resins and waxes has been proposed using either independently or in conjunction with HPC [33, 34]. Nevertheless, neither of these products demonstrated the ability to penetrate deep into the leather, besides the color alteration of leather after treatment and a rise in fragility. To tackle this issue, new collagen nanotubes were synthesized, implementing a conservation process capable of guaranteeing a long-lasting efficiency of the treatment, not modifying the leather appearance and internal fats equilibrium. The new nanomaterial exhibited an increment in flexibility, strength, and solubility in atypical solvents. The mechanical analysis revealed a high increment in tearing and tensile resistance, as well as in bending resistance, sufficiently significant to contrast the fragility of the original artifact, without generating rigid and brittle leather. Scanning electron microscope (SEM) imaging well displayed the capacity of nanocollagen solution to establish bonds among collagen fibers and to fill the cavities between them. Furthermore, subsequently, to nanocollagen application, the fibers appeared more untangled than previously, and the leather surface turned restored and smoother. The leather shrinkage temperature (ST) displays a noteworthy change within the application of nanocollagen solution: 47.6 °C before treatment, 59.6 °C after treatment. The shrinkage gap for the processed leather is shorter (ΔT 59.6–76.8 °C), indicating a risen uniformity in the arrangement and length of fibers. Moreover, the contraction starts at higher temperatures, proving the reconstruction of most of the collagen fibers. It should be noted that unbroken standard collagen usually starts its shrinkage roughly at ST 65 °C, a value not so far from the one achieved with the original leather treated with nanocollagen solution. This behavior can be disclosed as part of the reconstruction of the bonds through triple helixes and the network between them forming the quaternary structure of collagen molecule, besides a rehydration process [35].

Keratin

Keratin is a structural fibrous protein that makes up scales, hair, nails, feathers, horns, claws, hooves, and skin of vertebrates but also human hair. It is principally a compound of amino acid cysteine, which crosslinks through disulfide bonds creating filaments of a few nanometers in diameter. Keratin is incredibly insoluble in organic solvents and water.

Keratin was employed in hydrogels, nanoparticle formations, and biocompatible electronic devices. Since human hair contains keratin, it was used in the cosmetic field as UV-protective coating layers for the surface engineering of healthy human hair by using HNT/keratin or keratin/alginate/HNT suspensions in water. The proposed methods for human hair can be considered a resourceful protocol for the long-term protection of hair and textile in contemporary art. Indeed, the cysteine oxidation, by hair exposed to UV ray, was monitored to evaluate the protection capacity of the coating layer irradiation. HNT effectively enhanced the protective action of keratin to the hair structure, which is proven by AFM and dark-field hyperspectral microscopy. Furthermore, keratin/alginate/halloysite (HNT) hydrogel improved mechanical performances in terms of elasticity, strengths at yield, and breaking points (38%) of treated hair compared to the untreated one with stress at a breaking point of 23% [16, 17].

Similarly, HNT/keratin was proposed for consolidation and protection against UV irradiation damages of wool threads, made up of keratin (Fig. 3a). Wool thread samples are chemically compatible with the keratin coating, which acts as a reinforcing layer, and the use of HNT, attached on wool fiber scales as an anchoring site (Fig. 3b), improves mechanical resistance and UV radiation barrier (Fig. 3c) of wool samples. HNT/Keratin treatment did not alter the color of the wool sample and it was applied on a damaged wool yarn from a Flemish tapestry

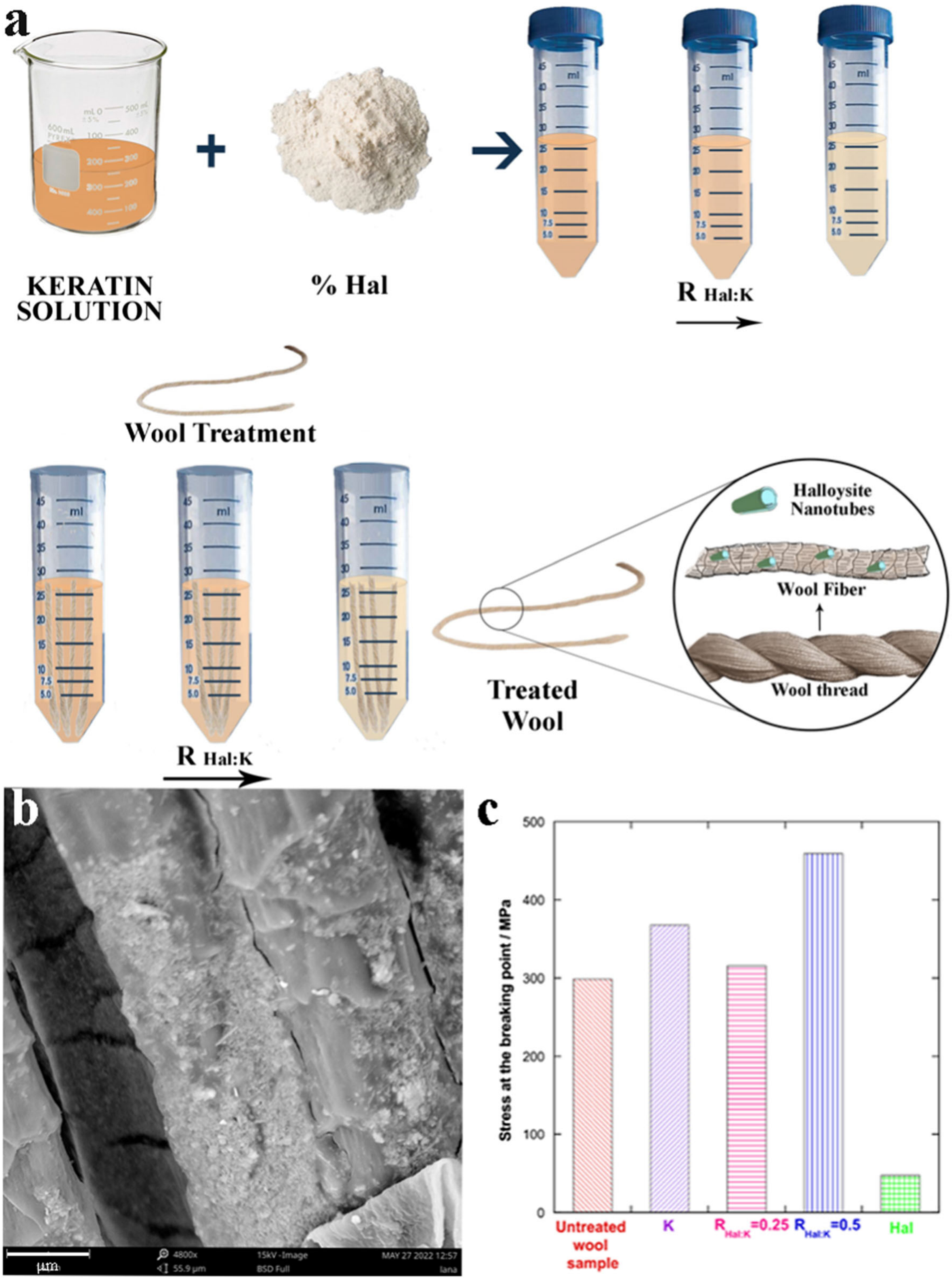


Figure 3 Hal/keratin protocol (**a**), SEM images of the wool sample treated R Hal:*K* = 0.5 (**b**), stress–strain curves of the treated sample (R Hal:*K*) compared to untreated sample (**c**) Reproduced with permission from permission [18]. Copyright© 2023 Elsevier.

(Sixteenth Century) achieving excellent results in terms of consolidation [18].

Polysaccharide-based biopolymers for consolidation treatment and protective coating

Chitosan

Chitosan is a cationic polysaccharide, and it has natural origin in animals. It is produced from the deacetylation of chitin, the second most abundant polysaccharide on Earth, a component of the skeletons of crustaceans but also mollusks, anthropoid insects. Chitin in an alkaline environment and with temperatures between 60 and 80 °C turns into chitosan, a linear polysaccharide consisting of D-glucosamine and N-acetyl-D-glucosamine. It has a less crystalline structure than chitin, therefore it is more soluble in reagents. The polymeric structural unit consists of an amino group, positively charged, which increases chitosan solubility in acidic aqueous solutions, and two OH groups, negatively charged, which are an attachment point for a substitution of a chain and the formation of newly derived polymers with different physicochemical characteristics suitable for biomedical and technological applications [19, 36–40].

S a consolidant treatment of waterlogged wood: chitosan showed the best treatment option in terms of quantifiable antibacterial efficiency, compared with CNC, PEG, and Alginate (Fig. 4). An important factor in choosing consolidants for archaeological wood, where the cellulosic component may be significantly reduced, is the capacity of the material to enhance the thermal stability of the lignin component. There was not a significant shift of the cellulosic peaks in the chitosan-treated samples; however, there was a marked difference in the lignin peaks, which shifted from 405 to 450 °C in the air-dried sample and 410 to 440 °C in the freeze-dried sample that suggests interactions of the chitosan with the lignin, improving its thermal properties to pre-degradation values. The degraded wood showed a lower cellulosic content so it is important to choose a consolidant that has a good affinity with lignin skeleton [41].

The antibacterial activity of chitosan is influenced by several factors including the species of bacteria and fungi, concentration, pH, solvent, and molecular weight. Chitosan can be improved by adding Ag-loading nano-SeO_2: crosslinked chitosan (CCTS), synthesized by an adsorption crosslinking reaction of monomers and catalytic alkoxides, with Ag-loading nano-SeO_2 (SLS), was tested on linen fabric, before and after aging treatment, as a consolidant. The antibacterial effect obtained against *E. coli and S. aureus* from 3 to 2 and from 7 to 4 h, respectively, confirming that CCTS–SLS had more powerful antibacterial activity due to the Ag-loading nano-SeO_2 that has excellent antibacterial and improving activity preventing from aging deformations for DMTA analysis but suffers from a color change.

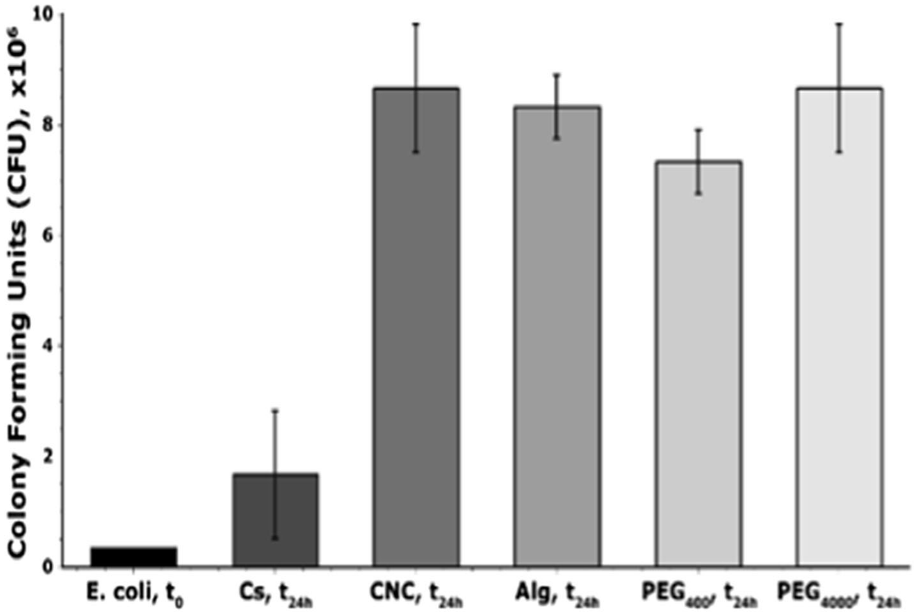


Figure 4 The graph shows the number of *E. coli* after 24 h incubation on archaeological wood treated with chitosan, CNCs, alginate, PEG400, and PEG4000 Reproduced with permission from [41]. Copyright© 2022 MDPI.

Chitosan was applied as an antibacterial coating film to protect cultural heritage, including a metal substrate, stone surface, and paper [42].

Nowadays, preventive conservation indicates treating metal substrates with a biopolymer matrix, loaded with chemically active compounds, such as corrosion inhibitors, a valid strategy for the protection of this artwork. Chitosan, soluble in water-based solutions is an eco-friendly material for the development of safe, green, and active protective coatings compared to commercial material coatings that use toxic solvents for the application. The effect of the type of acid used for chitosan dissolution, i.e., acetic acid (AcOH) and D-(+)-Gluconic δ-lactone (GDL), influences the quality of the films deposited onto the surface substrates and on the interaction of the polymer with the metal alloy. In particular, the use of GDL leads to high-quality chitosan films, since it does not cause the formation of Pb-based platelets, which were discovered in the presence of AcOH.

Moreover, the incorporation of benzotriazole (BTA) and 2-mercaptobenzothiazole (MBT) in the chitosan-based coatings improves their quality, anticorrosion properties, and removability, due to a synergic effect between the polymer matrix and the corrosion inhibitors, superior performance can be reached with BTA [43].

The research for alternative solutions has received increasing attention and several studies have addressed the use of less harmful compounds than BTA, such as imidazolium salt (IS) $HO_2CC_1MImNTf_2$. According to the analysis carried out on copper samples treated with chitosan (CHI), CHI/IS, CHI/BTA, and CHI/BTA/IS after treatment with Chloride Acid (HCl) in accelerating sample corrosion, IS is less effective than BTA in the protection of the bronze surface, but the use of $HO_2CC_1MImNTf_2$ in combination with BTA improves the protective efficacy of the CHI coating, showing a coactive effect of the two additives, gaining a less toxic protective formulation for the conservation of cultural heritage [44].

The biopolymer protecting properties were evaluated also on silver disks treated with chitosan, chitosan/BTA and compared with a commercial product, Incral 44: All silver samples, treated and untreated ones, were put into a wooden box, simulating the museums' storage, containing pieces of paper, leather, and plastic to estimate the coatings' effect on a real environment (Fig. 5). The films, after a long exposure (30 months), especially those

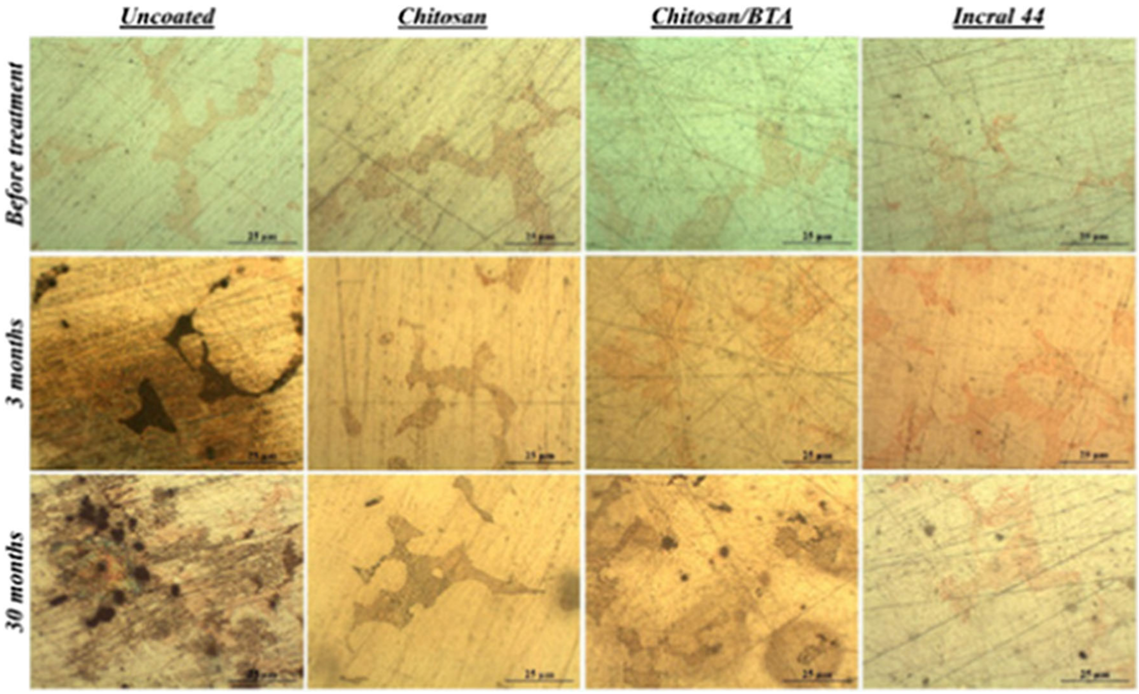


Figure 5 Silver disk surface, before and after treatment, detected at the optical microscope. Microscope images show different coating treatments, uncoated, chitosan, chitosan/BTA, and Incral 44: Each sample was exposed inside a wooden box at different times for 30 months Reproduced with permission from [45]. Copyright© 2022 MDPI.

containing benzotriazole, started to yellow due to the migration and nucleation of the silver nanoparticles inside the film-coatings, as revealed by the FE-SEM-EDS analyses and UV–vis spectroscopy. The pure chitosan film protected the silver surface from alteration [45].

Chitosan is a versatile material that can be used for many substrates, also as a coating layer for the conservation of paper-based artifacts by using nanomaterials technology: the goal for a researcher is to neutralize the acidity level of the paper gradually increasing as time passes and also for the presence of bacteria and fungi. In this case, Chitosan NPs (CS NPs) act as antimicrobial agents improved by the presence of calcium particles (Ca) and create a layer to reinforce the structure of the material to provide enhanced protection for paper-based documents. Ca/CS NPs generate a stronger inhibition effect on gram-positive bacteria and enabled pH stability [46].

At present, thanks to nanotechnology, it is possible to prepare a controlled release system for natural biocides by using Chitosan nanoparticles thymol-loaded for a protective layer on the stone surface. Nanoparticles improve the thermal stability and antimicrobial properties of chitosan. This innovative methodology solves the problem that natural essential oils are too volatile to use in outdoor stone cultural heritages and reduces the use of toxic biocides application [47]

The combination of chitosan (CHI) and hydroxyapatite (HAP) was studied for preventing salt crystallization damage in porous limestone samples. Hydroxyapatite (HAP) is used for the protection of carbonate stones to consolidate and protect from deterioration and damage of cultural heritage.

The coating HAP + CHI principally did not modify the porosity of the stone, demonstrating excellent compatibility, while they altered the capillary water absorption rate. Samples, treated and untreated, were exposed to a sodium sulfate solution to accelerate the salt crystallization cycles: HAP + CHI led to an enhancement in the stone resistance to salt crystallization, evaluated in terms of sample weight loss. Moreover, a positive effect in terms of mechanical properties was shown after HAP + CHI treatments on stone samples, specifically, there was a slight increase in the dynamic elastic modulus [48].

Cellulose

Cellulose and its derivatives are the most abundant and renewable polysaccharides available in nature. Cellulose consists of a linear polymer chain of several D-glucose units linked through β-1,4-glycosidic bonds and alternating regions of amorphous and crystalline zones, together forming the characteristic macroscopic fibrous structure of cellulose (Fig. 6). Cellulose is the main component of the primary cell wall of plants extracted from different natural sources, such as plants, straw (rice), algae, seeds (cotton), cane (bamboo, bagasse), small marine animals (tunicate), and some bacteria, with a high degree of purity. During the extraction, several processes are carried out for separating cellulose from the other components, for example hemicellulose and lignin, pectin, waxes, and other hydrosoluble components [49–51].

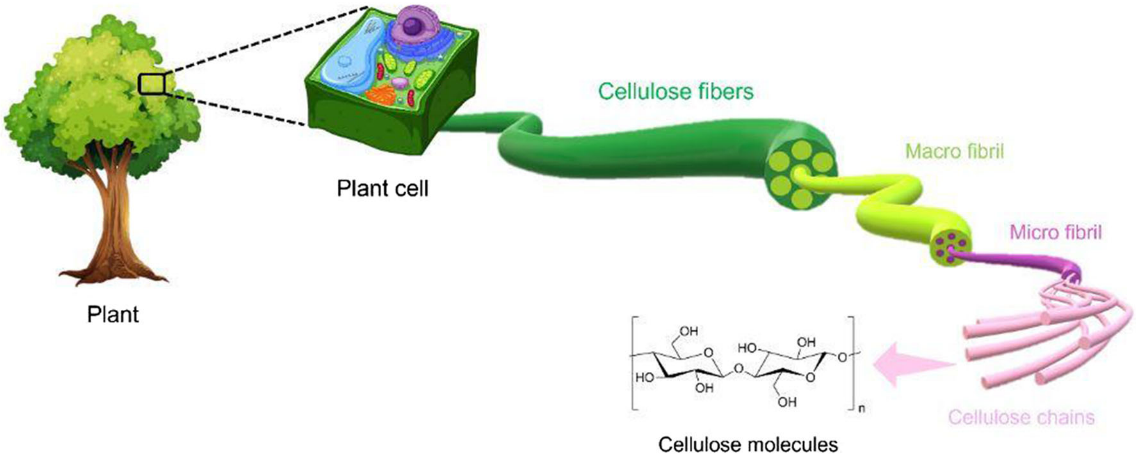


Figure 6 Structure of cellulose: from the plant to the chemical molecule Reproduced with permission from [49]. Copyright© 2014 John Wiley and Sons.

As an eco-friendly, renewable, biocompatible, high mechanical strength, and non-toxic material, cellulose finds its application in many fields, such as medical engineering, pharmacy, food industry, and also cultural heritage, due to the compatibility with many types of artistic substrates, which mainly consist of cellulose. All cellulose derivatives are an alternative solution to environmental pollution, non-renewable sources that are in continuous decline, global warming, and the energy crisis [50].

Hydroxypropyl cellulose (HPC) is an ether of cellulose in which some of the hydroxyl groups in the repeating glucose units have been hydroxy populated forming $–OCH_2CH(OH)CH_3$ groups using propylene oxide. HPC is a well-known material for paper consolidation in cultural heritage practices and the addiction of Halloysite nanotubes (HNT) on the HPC matrix is a promising consolidation treatment. HPC/HNT treatment increased the elasticity and the strength of the elongation of paper samples in terms of dynamic mechanical analysis (DMA) (Fig. 7). Moreover, the treatment changed the shape of the surface enhancing the roughness, so the paper surface hydrophobicity was increased [52].

Hydroxypropyl cellulose (HPC) is used also as a biopolymer matrix for nanocomposite coating on stone protection, due to the film-forming properties. Nanocomposite films were designed with wax/halloysite nanotubes (HNT) Pickering dispersed on the HPC matrix. Composite materials were applied on stone samples by different application protocols, brushing, and spraying and the presence of wax/HNT particles was detected with SEM analysis (Fig. 8a). The spray method leads to a better and more uniform coating compared with the brushing method, which is perfectly adherent to the substrate and more efficient as a protecting layer (Fig. 8b). However, brushing application affected the aspect of the surface as the color analysis indicates, despite the spray method. Both application methods increased the water contact angle of the treated stone sample, which turn into a more hydrophobic surface due to the presence of wax particles (Fig. 8c) [53].

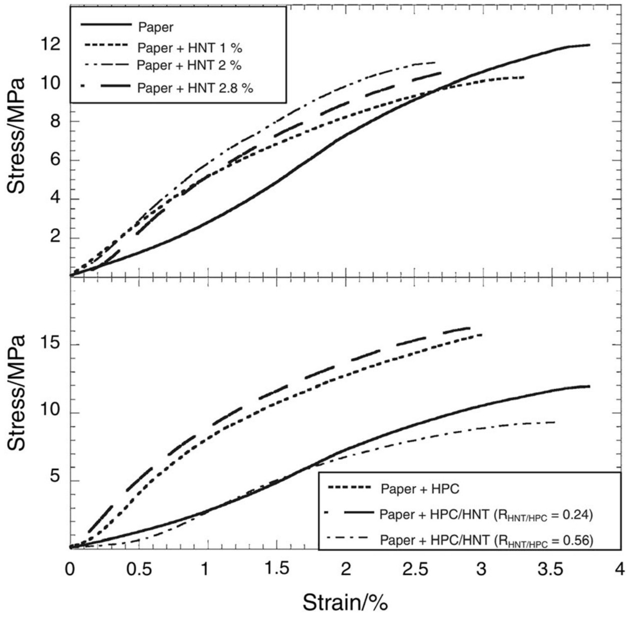


Figure 7 Curves of treated and untreated paper on DMA analysis Reproduced with permission from [52]. Copyright© 2014 Springer Nature.

Cellulose nanofibrils (CNF), cellulose nanocrystals (CNC), and lignin nanoparticles (LNP) have different nanoscale features, different morphologies, and advanced properties, which it is possible to take advantage of and applied as protective coatings onto wood and paper artwork thanks to the compatibility, stability, and renewability of nano-celluloses and nanolignins. The coating formulation was prepared by mixing CNF, CNC, and LNP at different percentage. LNPs protect the deterioration of coated substrates against UV rays. CNF/CNC mixture and CNF/CNC/LNPs mixture treatment on paper and wood samples do not alter the color of samples after the aging process compared with paraloid treatment that showed a $\Delta E > 8$ for paper samples. The coating treatment does not affect the surface properties of samples, certainly, morphology and roughness, as well as substrate vapor permeability, were mostly kept after the coating application. Nanocellulose/nanolignin coatings are reversible treatments, in addition they proved high durability, protective performance, and interfacial compatibility. Additionally, samples treated with a nanocomposite mixture showed a more controlled wettability with higher water contact angles compared with the untreated sample [54].

Cellulose nanocrystals, lignin nanoparticles, and bacterial cellulose (BC) are also used for consolidant treatments on waterlogged archaeological wood. Different species of waterlogged archaeological wood samples (oak, elm, stone pine, and silver fir) were impregnated with the consolidants. LNPs and BC treatments altered the color of wood samples. It is important to evaluate the penetration of the system

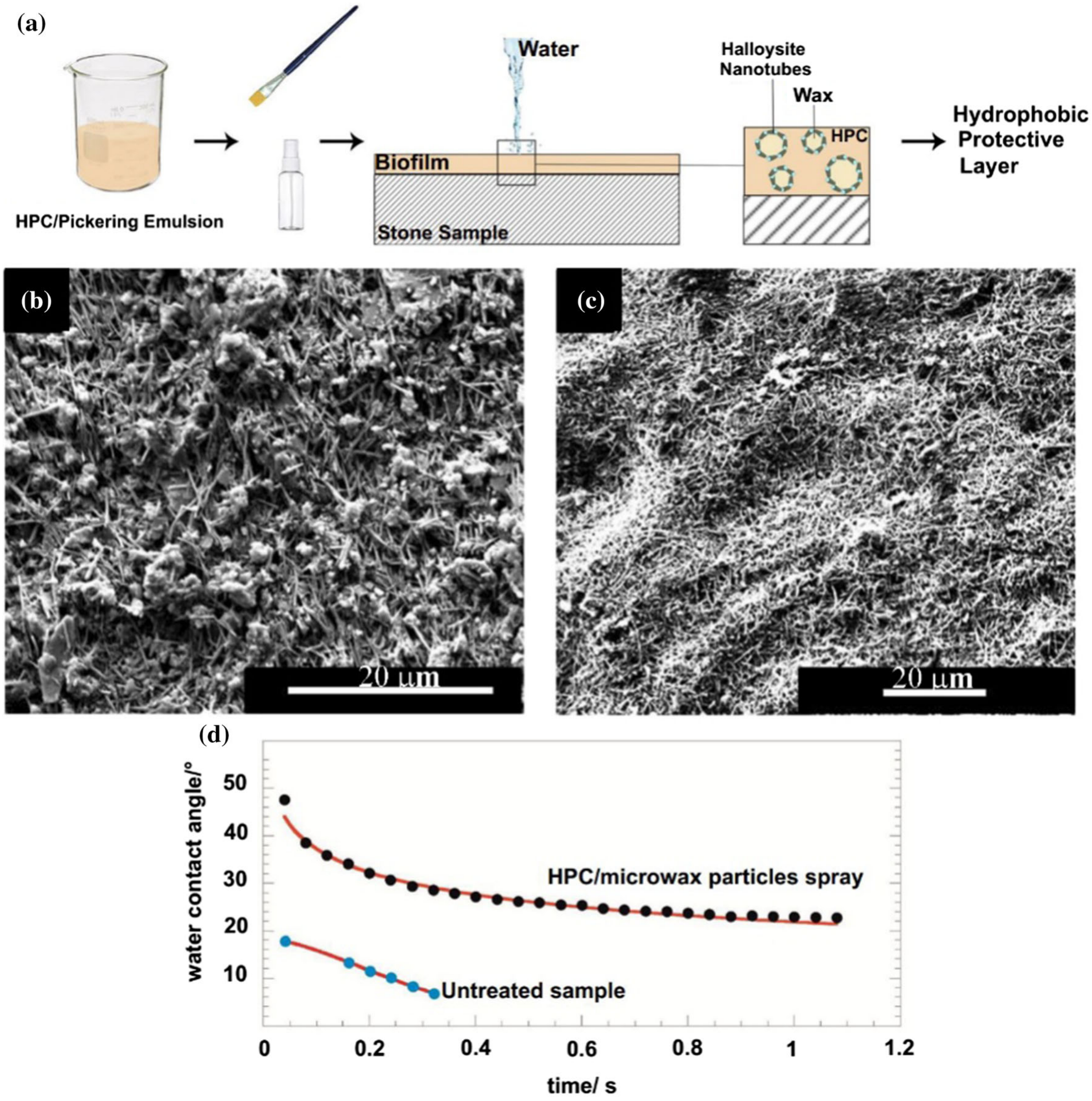


Figure 8 Draft (**a**) of Halloysite nanotube-based nanocomposites for the hydrophobization of hydraulic mortar. SEM images of stone surface treated with HPC and WAX/HNT composite films by spray (**b**) and brushing (**c**) application method. Water contact angle curves (**d**) of untreated stone sample and treated stone sample with HPC/WAX/HNT nanocomposite film by spray method Reproduced with permission from [53]. Copyright© 2021 Springer Nature.

on wood for the consolidation treatment: LNPs and CNCs treatment entered only about a millimeter inside the wood, although BC treatment formed a compact layer on the surface of the cell walls through the thickness of the samples, due to the chemical interactions between the nanoparticles themselves and between them and the wood. The CNCs impregnation bath became a gel during the treatment, probably nanoparticles interacting with each other form the gel consequently stopping successful penetration inside the wood sample. Despite the excellent result for the BC treatment on the diffusion process, the consolidation treatment was not efficient enough even if it was observed that whiskers operated as gap fillers interacting between each other and producing an open net structure inside wood tissues [55].

Cellulose has many derivatives, one of which is hydroxyethyl cellulose. The chemical structure of hydroxyethyl cellulose is similar to paper fibers; indeed, hydroxyl groups can form hydrogen bonds with the hydroxyl group on the paper fiber, so they have good compatibility and improve the mechanical strength and aging resistance of the paper. Hydrophobically modified hydroxyethyl cellulose-methyl methacrylate emulsion for paper protection was synthesized to improve the water-resistance and strength of paper. Methyl methacrylate has good thermal stability, active reaction activity, and good film forming. Hydroxyethyl cellulose-methyl methacrylate treatment on paper increases mechanical properties, according to machine direction (MD) analysis, specifically tensile strength of 92.91%, folding endurance of 508.4%, and tear strength of 52.44%. The treatment does not affect the optical properties of the paper and the paper preserves a network structure of fibers, giving good breathability, based on micromorphology analysis. Moreover, after 72 h of the aging test, mechanical properties decrease by 6% approximately, suggesting that the paper has some aging resistance. At the same time, water resistance was detected by contact angle measurement and treated paper showed a higher hydrophobicity [56].

The oxidative and acid-catalyzed degradation reactions are the main problems in the aging process of canvas that cause disruptions and cracks which compromise the paintwork of the entire picture. Two protocols for the deacidification and consolidation of canvas were performed:

- Hydroxyethyl methyl cellulose, derived from cellulose, and nanocrystalline cellulose in water act as consolidation components, and $CaCO_3$ particles in water outcomes as deacidification agents. Both materials have a polar character.
- Hydroxyethyl methyl cellulose and silylated nanocrystalline cellulose are the consolidation agents, while MgO particles dispersed in heptane act for deacidification. In this case, it is possible to avoid the risk of water-based products.

The two protocols were applied on an acidic model cotton canvas by brushing: these treatments, in both cases, allowed to enhance pH and deposit of an alkaline reserve into the canvas. The breaking force of the canvas increased by 17–38%, for the polar protocol and 36–42% for the nonpolar protocol. The stabilization effect is higher for the nonpolar system. It can be summarized that the stabilization effect after the silylation reaction is as good as for the polar nanocomposites and the interaction between the materials and the canvas is comparable. Both treatments showed a moderate yellowing effect on the cotton canvas surface and aged canvases exhibiting a slightly darkening for the polar treatments, due to the dilution of polar contaminants where water tends to swell the cellulose fibers, and a slight whitening for the nonpolar treatments. After the aging process, the breaking force of the treated canvas samples was still higher than the untreated, not aged canvas: The breaking force for canvas treated with nonpolar protocol increased by 55.5%. Both systems can be used for deacidification as a preventive measure for the protection of canvas [57].

Pectin

Pectin is a biopolymer from plants. It has an anionic polysaccharide structure contained in the cell walls of plant tissues, as well as apple pulp and citrus peel. Pectin is formed mainly by a linear chain of D-galacturonic acid linked by α-1, 4 glycosidic bonds, and it has hydrophilic nature with numerous carboxylic groups, negatively charged. The presence of a negative charge group facilitates the interaction of pectin with metal cations and active molecules. This biocompatible and eco-friendly polymer was used to form gels and films for agriculture and food industry, being an edible and safe material [19, 58]. It is also used for cultural heritage as a gel for cleaning or a coating film.

Regarding the latter, a pectin matrix loaded with wax/HNT Pickering is a novel promising protocol for the protection of surface artworks from the aging process due to environmental conditions. The colloidal stability of the nanocomposite system, wax/HNT Pickering emulsion, was improved by pectin, based on macroscopic observations. The composite film was designed by solvent casting method and the contact angle analysis exposed a significant hydrophobization of the biopolymeric film (77.6 and 88.4° for pectin and pectin/wax/HNT, respectively) (Fig. 9). The DMA analysis highlighted an important enhancement (109%) of the elastic modulus of the pectin/wax/HNT film, on the other hand, the stress at the breaking point for both film, pure pectin and pectin/wax/HNT, is analogous with values of ca. 55 MPa [59].

PEC/CHI film, by adding HNT as a carrier for antioxidants molecules (vanillic acid and quercetin), is a promising mixture for cultural heritage protection. Water contact angle values of film decrease with the presence of HNT, in addition, it should be noted

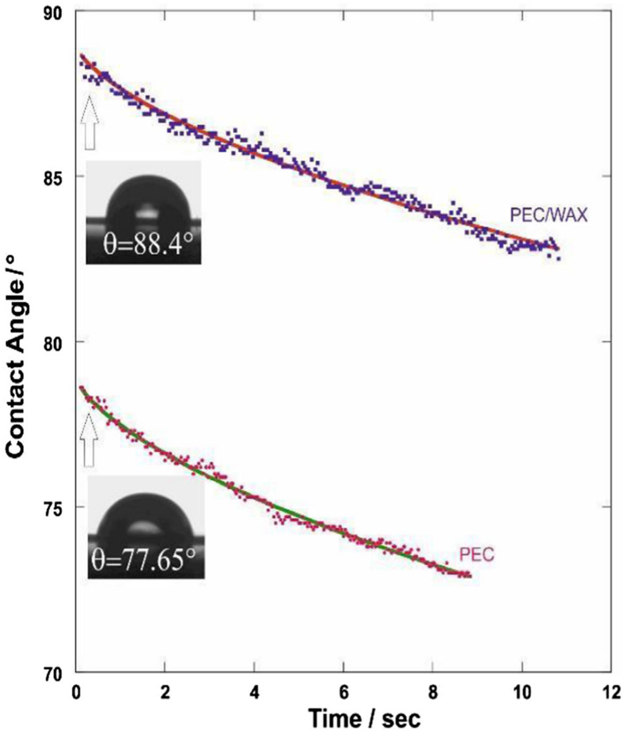


Figure 9 The graph exhibits the kinetics of water drop on composite film: the contact angle of water drop on composite film PEC/WAX is higher (ϑ = 88.4°) than the angle on pure pectin film (ϑ = 77.6°) Reproduced with permission from [59]. Copyright© 2023 Elsevier.

that antioxidants in HNT do not further alter the film wettability. Antioxidant molecules establish protection action on the artwork surface, indeed HNT, making the PEC/CHI films ever more resistant to photo-oxidation, appropriate for cultural heritage protection [19]. PEC/CHI films can be enriched by adding crosslinking, citric acid (CA), and reinforcement agents, HNT, to have a beneficial effect on the film performance. CA supports the formation of crosslinked structures, and HNT allows to improve the rigidity of the biopolymer films and absorbs efficiently the UV irradiation [60].

Funori

Funori (or funoran) is a polysaccharide derived from the red algae genus *Gloiopeltis*.

Depending on the extraction specie, we can distinguish three different types of funori changing in structure: fukuro-funori, ma-funori, and hana-funori extracted from *Gloiopeltis furcata*, *Gloiopeltis tenax*, and *Gloiopeltis complanata*, respectively. Among them, the first two types are well known to be very efficient as consolidating and adhesive agents. It is a galactan sulfate, whose main chain is composed of alternated repeating units, (1,3)-β-Dgalactopyranose, linked to (1,4)-α-(L or D)-galactopyranose [61]. Funori is a red seaweed belonging to the Rhodophyta family, together with agars, carrageenans, and porphyrans. Although it is classified as a type of agar, Funori has chemical and structural properties more similar to carrageenans. Indeed, it is sulfated as carrageenans, even if with a lower degree [62, 63].

In Japan, it has been used long in the medicine and food industry, or as a cultural heritage conservation material due to its thickening and adhesive properties. This seaweed product originally used over 300 years ago continues to be produced and used today for the conservation of several artifacts, competing with many other synthetic conventional products boasting a non-toxic form [64]. The advantages of using Funori are its low surface tension, strong penetrability, high wettability, matt finish drying, and non-toxicity. It is generally employed as a mild consolidant for paper, painting layers, and gold or silver leaves, where a weak binding is required [65, 66].

A noteworthy use of Funori in the cultural heritage conservation field is its application combined with $Ca(OH)_2$ nanocrystals as an alkaline tank to prevent and contrast the possible acidification processes which cause the depolymerization of cellulose. Textiles samples of aged linen yarn were treated employing Funori with and without $Ca(OH)_2$ nanocrystals. Tensile strength analysis was carried out, showing an increment in strength for all the consolidated samples (Fig. 10). This new system displayed optimum performance, revealing new perspectives for the preventive conservation field since the innovative material at once prevents degradation and consolidate [67].

The area where Funori best applies is paper conservation, including those stiff to those thin, and more degradable. As revealed by SEM/EDS microscopy technique, Funori is a good match for cellulose fibers. The fraying behavior recorded for some samples slowly disappear increasing Funori application and observing the adhesion of one fiber to another. Even mechanical analysis confirmed the good Funori consolidation power: Higher tensile stress and strain at the breaking point are achieved by increasing the treatments from three to six, obtaining a more extensible and thicker paper. Moreover, any color changes on paper are not recorded [68].

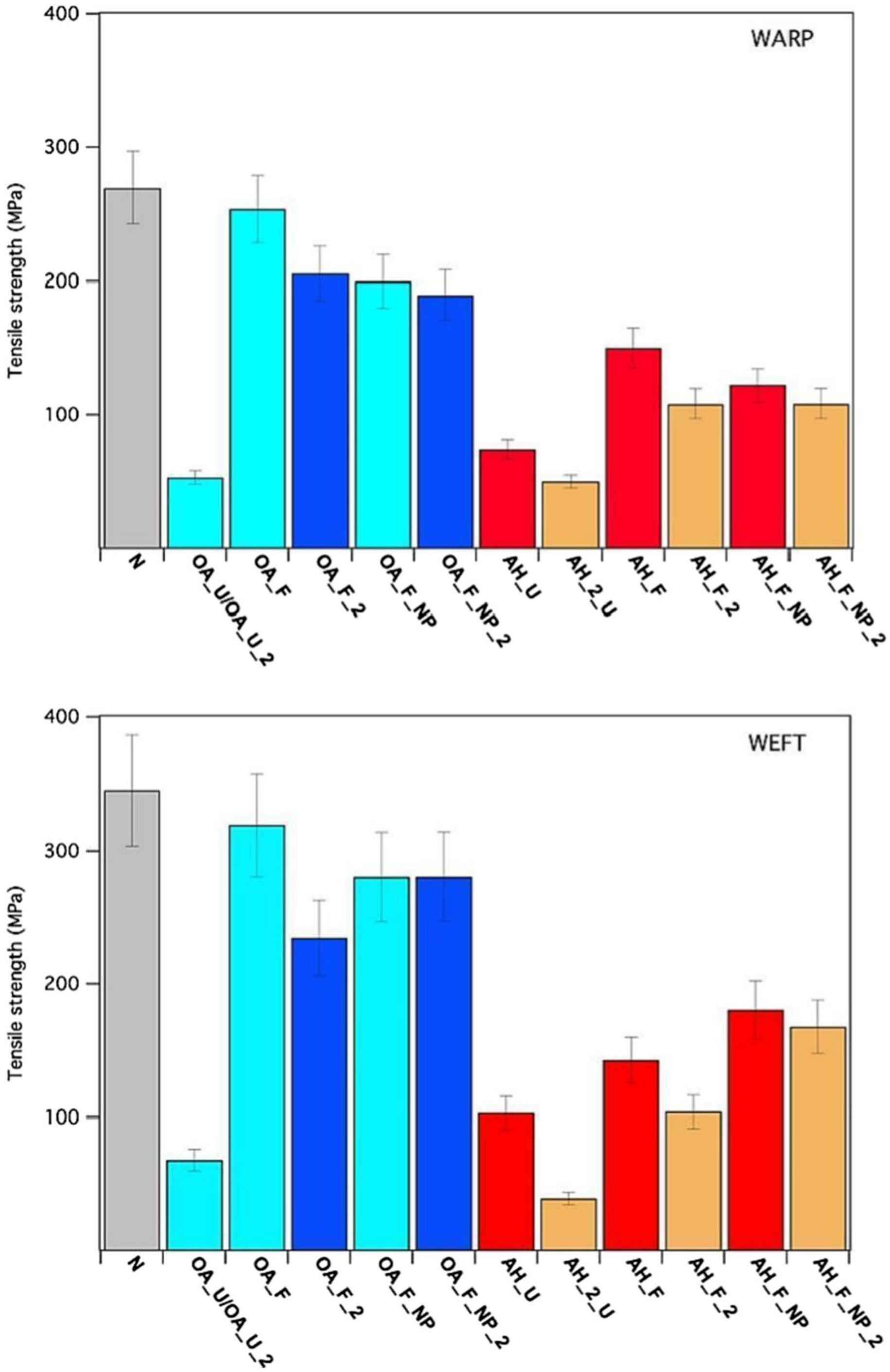


Figure 10 Tensile strength (MPa) of the linen warp (top) and weft (bottom) aged, treated, and not treated by different consolidants. Acronyms: *F* = Funori; *U* = Untreated; F_NP = Funori and $Ca(OH)_2$ Nanoparticles; *N* = not aged; OA and AH refer to the aging procedure. 2 indicates the second AH or OA aging treatment Reproduced with permission from [67]. Copyright© 2023 Elsevier.

Another area of wide application is the use of Funori as a consolidation of pictorial layers on the canvas. By comparing and testing it with Aquazol® 200 and 500, traditional adhesives used for consolidation, Funori was confirmed to be a stronger binding agent, even at lower concentrations in deionized water than the concentrations of the other resins in their solvents [13]. Research into new consolidants for matt paint is gaining ground to evaluate their usability finding a product that does not affect aesthetic appearance. For this purpose, Funori was compared with sturgeon glue, Klucel E, and gelatin. In particular, under the same conditions, after Klucel E application a darkening of the surface is recorded, while Funori showed good stability even after UV aging and variations of temperature and humidity. In addition, the viability test showed that Funori has greater resistance against biological attack [69].

Subsequently the evaluation of differences in painting surface color after consolidation treatments and aging tests, Funori recorded the best results if compared with other synthetic adhesives, such as Gelvatol or Acril 33. These materials resulted in more sensitivity than Funori to the ultraviolet light used in the aging treatment, producing changes visible to the human eye [70].

Furthermore, Funori has also found applications in wall painting consolidation, showing an excellent affinity to the inorganic support. Indeed, the efficiency of consolidation was suitable as well as the preservation of the plaster's porosity and water vapor permeability. Despite being a hygroscopic material, after humidity variations, no changes in the consolidated surface are recorded. Instead, the increasing viscosity of Funori solution which occurs if soluble salts are present may be a limit. Especially in the presence of potassium and sodium salts, common in wall paintings, Funori starts gelling without properly penetrating inside the substrate. Moreover, an excess of material on the surface can cause a reduction of plaster's water vapor permeability. Excluding the salt-contaminated samples, in each case the painting layers' cohesion improved. As far as concern biological resistance, we can assess that Funori can be used in outdoor environments because it did not show any microbial growth [71].

Sodium alginate

Alginate, an anionic polysaccharide, derives from cell walls of brown marine algae, i.e., *Macrocystis pyrifera, Ascophyllum nodosum, Laminaria hyperborean.* Alginates are salts of alginic acid (AA) and depending on the source, the chemical structure of alginic acid may differ but it is constructed by a sequence of L-guluronic and D-mannuronic acid residues with different amounts and geometries. Sodium alginate is the most common derivative of alginic acid resulting from the treatment of alginic acid with mineral acids. Sodium alginate is known for its low toxicity, biocompatibility, and solubility in water at neutral and alkaline conditions due to the presence of carboxylic groups in its structure. Sodium alginate was studied as a smart nanocarrier for drugs delivery for its release ability in response to pH increase [27], but it is also known for its capacity to form hydrogel and film as bioactive components that can be used for the fabrication of antimicrobial composite coating for stone artworks on cultural heritage[72, 73].

It developed an antimicrobial organic oxidized sodium alginate (OSA)/inorganic calcium phosphate oligomers (CPO)/zinc oxide (ZnO) NPs material for protecting the historic stone surface from microbial biofilms. ZnO NPs have been chosen as antimicrobial agents for their high stability, low cost, and great biocompatibility with cultural heritage and for human health. OSA allows stability and anchoring sites for hydrophilic ZnO NPs by developing a Schiff base (Fig. 11). Moreover, OSA-built units bond via electrostatic attraction with CPO, consequently there is an increase of the bonding between the antimicrobial agents and the affected stone substrate [74].

An alternative material to ZnO NPs, to prevent the risk of paper and wood artwork being gradually damaged by chemical and biological enemies are

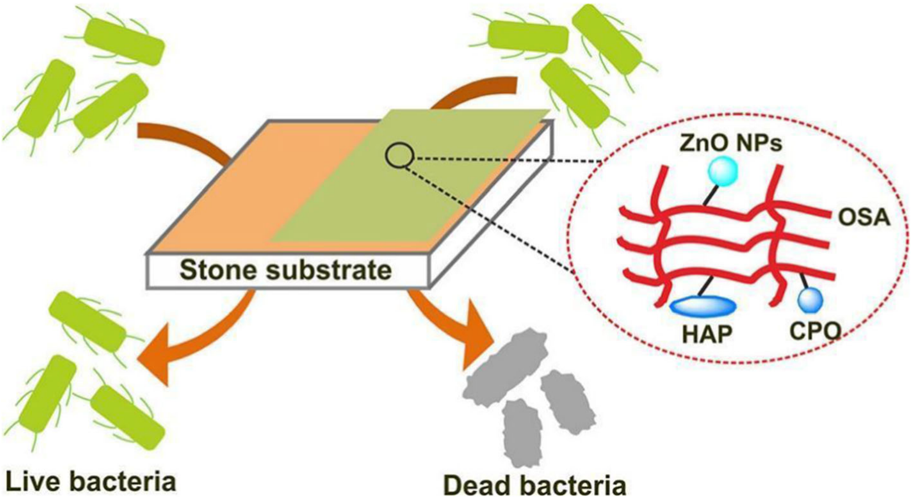


Figure 11 Schematic sketch of composite coatings ZnO nanoparticle-based/OSA/CPO as an antimicrobial and hydrophilic layer for Sandstone heritage conservation Reproduced with permission from [74]. Copyright© 2021, American Chemical Society.

essential oils. Cinnamon essential oils have been incorporated into sodium alginate spheres and psyllium-alginate mixtures spheres. The presence of essential oil inside beads was confirmed from gas chromatography analysis: In particular, psyllium-alginate beads contain a large amount of Cinnamaldehyde and Linalool, a component of Cinnamon essential oil. The release of essential oil from beads was studied by respirometry tests on Saccharomyces cerevisiae, based on the decreased breathing capacity. The roughness of the sphere surface can affect the release of essential oil; indeed, it was rapid the first time (5th day), then the essential oil release became slow with the increase of roughness. Therefore, a lower trend from aggregates and a significant release surface were shown. Better success was attained with the psyllium-alginate beads in the encapsulation and the essential oil-releasing process if compared with that one of only alginate [75].

Conclusions and perspectives

In this review, several biopolymers were presented: gelatin, collagen, chitosan, and fibroin, from proteins' natural source and pectin, lignin, cellulose, and derivatives, alginate, and Funori, from polysaccharides source. The structure and properties of each biopolymer were first shown. These materials are commonly available, biocompatible, non-toxic, biodegradable, edible, transparent, and can be easily functionalized. Biopolymers are promising components for smart solutions in the field of the conservation and restoration of cultural heritage as good substitutes for synthetic products used for consolidation and protection treatment.

It is well known that chitosan has an antimicrobial property that makes it a perfect polymer to protect cultural heritage, including a metal substrate, stone surface, and paper. Chitosan matrix can be modified by adding calcium particles (Ca), Ag-loading nano-SeO_2 (SLS), hydroxyapatite (HAP), and imidazolium salt (IS) to improve antimicrobial properties of polymer and enhancing consolidation capacity of treatment for different surface artwork.

Film-forming properties of biopolymers lead to the design of a composite layer with active compounds that can interact with many materials such as paper, wood, stone, fiber, archeological wood, canvas, textile, and painting, by increasing strength and cohesion of damaged artwork for the consolidation treatment and by protecting the surface from the natural agent that can cause artifacts deterioration.

A good strategy is to use the same based materials of which are made artworks without altering the chemical composition and giving back the aesthetic aspect of the work. One example is the fibroin used to consolidate silk artifacts that influencing the mechanical properties of samples or collagen for treatment of leather without modifying the leather appearance and internal fats equilibrium.

Nanocellulose/nanolignin coatings are used for consolidation treatment of paper and treated sample showed a more controlled wettability with higher water contact angles.

Nanomaterials are progressively taking the place of synthetic resins frequently used as consolidants or coating, thus providing better results both in terms of mechanical properties and stability toward moisture changes; therefore, incorporating nanomaterials allowed a very innovative approach to improving biopolymers' properties.

Sodium alginate was developed with inorganic calcium phosphate oligomers (CPO)/zinc oxide (ZnO) NPIt for protecting the historic stone surface from microbial biofilms.

$Ca(OH)_2$ nanocrystals on funori matrix were used as an alkaline tank to prevent and contrast the possible acidification processes for the treatment of paper artwork.

Nanoclays are one of them, they can stabilize a mixture of water-based biopolymer solution, enhancing the thermal and mechanical properties of biopolymers, besides modifying the colloidal stability of the mixture. For example, halloysite nanotubes allowed to create wax microparticles on pectin or HPC matrix for treating stone surface and creating a hydrophobization layer.

The application of halloysite nanotubes effectively enhanced the protective action of keratin to the wool samples as UV shielding and improves mechanical resistance as reported in literature.

The same results were evidenced on HPC/HNT treatment where the elasticity and the strength of the elongation of paper samples were increased in terms of dynamic mechanical analysis.

The addition of specific metal nanoparticles in the biopolymer mixture acts as antibacterial activity, therefore impeding degradation due to the development of mold and bacteria attacks, or also UV light protection.

Nowadays, essential oils are widely investigated as natural sources of active agents against bacteria, fungi, and biofilm, which often is the main problem for artwork. Essential oils as antibacterial materials enhance the properties of protecting treatment and avoid the application of antibacterial agent that is dangerous for both humans and the environment.

It was demonstrated that citronella oil is used on gelatin as an antimicrobial agent for the consolidation treatment se of gelatin as adhesive and consolidant.

It is also possible to add different active molecules on consolidating or protective biopolymer-based protocols for deacidifying action without affecting the aesthetic aspect of the artwork such as calcium carbonate or magnesium oxide nanoparticles.

The physicochemical properties of proteins and polysaccharides makes them an appropriate matrix to design complex hybrid structures with inorganic materials and active molecules for advanced application in consolidation and protecting treatments on wood, paper, metal, canvas, and stone artwork.

The future challenge of this research concerns the study of new systems of biopolymers, nanocellulose, improved with active molecules, essential oils, and nanomaterial, naturally taking into account the "green" aspect and thus the eco-sustainability and biocompatibility to use these new products aimed at restoring the cohesion of the material and protective solution for artworks and to avoid synthetic material harmful for both humans and the environment.

An interdisciplinary research work leads to the study and enhancement of biopolymers with a low environmental impact and advanced technological content for gradually innovative and sustainable applications on cultural heritage to preserve artwork as long as possible.

A suggestion for future research is to create hybrid dispersion composed of different biopolymers with the addition of essential oils and nanomaterials that led to high improvements, outperforming the single component dispersion at the same concentration by enhancing physicochemical properties of materials for different treatments.

As a final observation, throughout the years, the scientific community highlight a greater sensitivity towards reversibility and non-toxicity of materials to be used on cultural heritage. Subsequently, it is important, when introducing protective coatings and consolidation material in the conservation application, to define a protocol that respects some characteristics: reversible, non-toxic, eco-friendly, compatible with the substrate, easy to remove, and low cost. Before starting to design new protective and consolidation coatings, a preliminary step must be done: the evaluation of the damage on surface artwork to define the conservation status and to identify the degradation problems. Once, selected the most suitable biopolymer for the artwork surface and the nanomaterial or active molecules, it can be characterized. Finally, the application of artificial samples and the aging experiment must be done to validate the coating and consolidation treatments' durability and removability.

Further biopolymers applications on cultural heritage artworks are still being developed.

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Author contributions

MRC and GD were involved in investigation, and writing-original draft preparation. SM was involved in conceptualization, and supervision. GC was involved in writing-reviewing and editing, and validation. GL: was involved in funding acquisition, and resources.

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Data and code availability

All the data will be provided to the readers on request.

Declarations

Conflict of interest The authors declare that they have no conflict of interest.

Ethical approval The work does not report any experiments involving human tissue that require the approval of an institutional review board or equivalent ethics committee.

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