Advances in Historical Wood Consolidation and Conservation Materials

Qi Wang, a Xinhao Feng, a,b,* and Xinyou Liu a,*

Wood is an indispensable renewable material for national economic development. As a bio-organic material, wood is subject to deterioration due to climatic, biological, and chemical factors, which greatly limit the advantages of wood products and increase the difficulty of conserving historical wood. To preserve the historical and cultural heritage, extend the historical life of ancient wooden structures, and promote the efficient and sustainable utilization of wood resources, this paper provides an overview of the main degradation and destruction forms and biochemical changes of wood in ancient architecture, unearthed relics, and antique ship wood from the perspective of wooden structure, historical applications, and their forms of destruction. The conservation strategies and consolidation methods of ancient wood are reviewed, with emphasis on the summary and analysis of the properties and uses of different consolidation materials and their methodological characteristics for the conservation of historical wood. In the context of the development of biomaterials, polymer chemistry and nanotechnology, biomass nanocomposites are applied gradually in the field of consolidation. To provide a strong basis for the effective use of reinforced wood, this paper presents the theoretical foundation for the research and development of green, efficient, and environmentally friendly wood consolidation and protection technologies.

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Contact information: a: College of Furnishings and Industrial Design, Nanjing Forestry University, Nanjing 210037, China; b: Jiangsu Co-Innovation Centre of Efficient Processing and Utilization of Forest Resources, Nanjing 210037, China; *Corresponding author: fengxinhao@hotmail.com (Feng, X); liu.xinyou@njfu.edu.cn (Liu, X)

INTRODUCTION

Wood is a natural polymer material that has evolved biologically over a long period of time. Due to its easy accessibility and the excellent stability of its structure, wood has been widely used in construction, practical tools, transportation, and decorative items since the beginning of human civilization; it has had major contributions to the development of society (Florian 1989; Li 2014; Chen et al. 2020). In today's quest for social sustainability, a variety of factors are driving the utilization of wood even more. However, owing to its biological nature, it is subject to damage via various external factors in the process of use, such as aging and degradation, fungal degradation, and insect infestation. This has led to its performance deterioration, service life reduction, reduced utilization value, and other problems. Therefore, the study of wood resources is not only beneficial to the advancement of humanities and social sciences, but also provides vital data and information for the study of materials and other engineering disciplines (Walsh-Korb and Avérous 2019).
Historical wood consolidation is a specialized and systematic discipline at the intersection of archaeology, wood science, chemistry, biology, and other disciplines; it focuses on the nature of wood, mechanisms of degradation and deterioration, and conservation consolidation (Fratzl and Weinkamer 2007; Gibson 2012; Janusz et al. 2017; Ghavidel et al. 2020). Meanwhile, the current common wood consolidation methods and chemicals are somewhat defective while working, and more research is needed to identify better materials in the future (Cocca et al. 2004; Christensen et al. 2012; Kennedy and Pennington 2014; Spinella et al. 2021). For ancient architecture, unearthed cultural relics, and underwater ancient ships and other wooden relics, consolidation reagents are being used to improve the mechanical properties and dimensional stability of historical wood based on avoiding its biological or non-biological degradation damage as far as possible. Especially for the specificity of historical wood, conservation ethics emphasizes the reversibility of the consolidation material and the scope for further treatment in the future.

This review summarizes research progress in the conservation of historical wood and the characteristics, advantages, and disadvantages of consolidation materials, providing a reference basis for the conservation of wood resources and the selection of consolidation materials. The consolidation and restoration of historical wood will improve the efficient use of wood resources, reduce the carbonization rate to a certain extent, and provide strong technical support for the forest industry to achieve the goal of “carbon peaking and carbon neutrality”. The road to the preservation of wood products is long and difficult, which is the continuation of human civilization and is of great significance to the Chinese nation and even to world culture.

DEGRADATION FORMS OF HISTORICAL WOOD AND CONSERVATION STRATEGIES

Historical wood (or “archaeological wood”) shows evidence of having been used by human civilization or has been left unaltered and discarded in its natural environment, and is of historical and cultural value (Florian 1989). Wood runs through the historical process of human civilization, and the structures and products, typically represented by buildings and furniture, have been developed over thousands of years and are closely related to human production and life.

The early use of wood was primarily to meet social needs. In China, wooden objects and furniture such as plates, benches, and “zu” (ancient sacrificial utensil or vessel/chopping block) were used during the late Neolithic period. Wood may have been used earlier than the wooden spears of the Paleolithic (ca. 400,000 years ago) (Ambrose 2001; Harmand et al. 2015; Wu 2021). Because of its stiffness, strength, and stability, it has been used in the construction of transport and residential objects such as ships and buildings, with the oldest surviving wooden ships tracing back to the Mesolithic period in 7500 BC (Bednarik 1997). The used of wood as a building material has lagged behind, but has also occurred for thousands of years. Structures such as China's traditional “tailiang” (lifting beams) and “chuandou” (post-and-tie construction) are an important part of human civilization and demonstrate superb building techniques and unique artistic styles (Yu et al. 2017). Ancient wooden architecture, unearthed wooden artifacts from excavations, salvaged ancient ships, and wooden products are the main sources of historical wood.
Wood Structure

As a natural polymeric biomass composite material, wood has a multi-level cell structure and composition with distinctive heterogeneity, mainly including cellulose, lignin, hemicellulose, etc. (Sjostrom 1993; Ling et al. 2018). The hierarchical structure of wood is reflected in the several length scales, as shown in Fig. 1, from the macroscopic structure of the trunk to the micron scale of the cell wall, to the nanostructures of lignin, hemicellulose, and cellulose chains (Fratzl and Weinkamer 2007; Weinkamer and Fratzl 2011; Ling et al. 2018; Chen et al. 2020).

![Hierarchical structure and anisotropy of wood, from macroscopic to molecular scale.](image)

Fig. 1. Hierarchical structure and anisotropy of wood, from macroscopic to molecular scale. Reprinted with permission from Chen and Hu (2018). Nanocellulose toward advanced energy storage devices: Structure and electrochemistry, Accounts of Chemical Research 51(12), Copyright 2018, American Chemical Society.

The cells that make up wood vary in type and size, but the cell tissue in each hierarchical unit provides functions such as mechanical support, material transport, and storage (Fratzl and Weinkamer 2007; Berglund and Burgert 2018). The morphology of the wood cell wall plays a decisive role in its properties, so wood conservation and consolidation treatment are inseparable from cell wall characteristics. Wood cell walls are composed mainly of three biopolymers, cellulose, hemicellulose, and lignin, which form a composite material based on natural fibers (Fahlén and Salmén 2003; Berglund and Burgert 2018). Cell wall tissue structure is based on cellulose as the skeleton, which is closely combined with amorphous hemicellulose to form a microfiber network. Lignin surrounds the cellulose microfibrils, and pectin forms a hydrogel that bonds cell wall components in the form of cross-linked polysaccharides. The interactions between cellulose, hemicellulose, and lignin have important effects on cell wall properties, but no direct crosslinking between cellulose and lignin has been observed.
The wall structure consists of primary wall, secondary wall, and intercellular layer (lumen), and each part is secreted by protoplasm over time such that the oldest primary wall, as the first solid cover of new cells, is farthest from the protoplasm and is located at the outermost part of the cell wall, etc. (Gibson 2012). The primary wall contains cellulose microfibrils in the form of intersecting fine aggregates, which can promote cell diameter increase and lignification when new cells mature (Fry 2004). The secondary wall is divided into three layers, S1, S2, and S3 (Gibson 2012), composed of various thicknesses and compositions of crystalline cellulose complex embedded in a lignin and hemicellulose matrix. The S1 layer is composed of several thin layers of flattened helical microfibrils that form a cross structure that is vital for the compressive strength of the cells. The S2 layer is the thickest of the secondary walls, accounting for more than 95% of the cell wall thickness, and has the highest fiber content. Therefore, the S2 layer significantly affects the mechanical properties of the cell wall and has a supporting and protective role for the wood. Unlike the other two layers of fiber alignment, the cellulose nanofibers in the S2 layer have a large helix angle and are almost perpendicular to the cell axis, resulting in anisotropy (Fratzl and Weinkamer 2007). Indeed, anisotropy is more prominent in earlywood because the wood cells grow faster and are larger in spring when the growing conditions are good (Unger et al. 2001). As for the S3 layer, the orientation of cellulose microfibrils is still undetermined, and it has been suggested that other cells may be present in the parenchyma cells to replace the S3 layer (Gibson 2012).

In addition to the general characteristics of wood structure, differences in cell type, size, and wall cavity ratio also lead to variation in wood anatomical structure. Changes in the chemical composition of wood can also contribute to a diversity of properties such as color, odor, and durability. Because of the variation that wood exhibits at different scales, its effective conservation and consolidation must start at the cell wall to achieve the structural improvement and functionalization of wood radically (Chen et al. 2020).

**Historical Wood and Its Degradation Properties**

The structure and nature of wood are such that it is inevitably subject to the synergistic effects of many factors, such as ultraviolet light, temperature and humidity, weathering, fungus, bacteria, and acid and alkaline salts. All of these can lead to the destruction of the natural structure and components of wood, including the macrostructure, microscopic cell wall structure and ultramicroscopic wall structure (Rowell 2012), resulting in a shortened life span and reduced performance. The macroscopic structures of ancient architecture wood, unearthed artifact wood/underwater ancient ship wood damage under the coordinated effect of multiple factors are shown in Fig. 2 respectively. At the molecular scale, the corrosion mechanisms of various factors are similar, mainly involving hydrolysis of acetal bonds in polysaccharides, various redox and radical reactions of carbon, ester and ether bonds in the aromatic structure of lignin (Broda and Hill 2021). The degradation of wood in ancient architecture and unearthed artifacts depends on its biological and chemical properties. The main chemical components in its cell wall do not degrade rapidly in a short period of time, but over time, microbial and acid-base hydrolysis will continue to drive this process, which in turn affects the cell wall components and destroys its structure (Klaassen 2008).
Wood degradation forms of ancient architecture and its structure changes

As the main component of ancient architecture, wood is prone to cracking, decay, and insect infestation due to its own biomass material characteristics (Ridout 2001). Yuan et al. (2021) showed that the wooden structure of ancient architecture are in varying degrees of damage, accounting for the highest percentage of damage in the form of cracking. Most of the damage to wood structures is due to the destruction of the wood itself, but corrosion is one of the more serious hazards of many mutilations.

Architecture is exposed to the natural environment for a long time, and microstructures such as wood cell walls are mainly subjected to fungal biodegradation. Fungal degradation of wood is produced by breaking down the extracellular enzymes of its wood cell walls and is mainly classified as white rot, brown rot, and soft rot according to the visual characteristics of wood degradation (Fig. 3) (Singh 2012). The white rot and brown rot fungi of the Basidiomycota are the major decay fungi of ancient architectural wood components (Francis 2007; Cragg et al. 2015). White rot fungi are mainly found in broad-leaf wood and can decompose lignin and other phenolic compounds. Because white rot fungi degrade lignin more than cellulose and hemicellulose, it is more likely to leave spongy white spots and other property changes in the decayed area (Stokland et al. 2012; Ge et al. 2017). Under their attack, the first to be destroyed is the secondary wall in the cell wall structure, followed by the degradation of the primary wall and intercellular layer in turn, so the cell wall delamination and detachment, resulting in aggressive wood damage (Daniel 2016). Brown rot fungi are common in coniferous wood, mainly decomposing cellulose, hemicellulose, and other sugar substances. They will preferentially degrade the S2 layer without destroying the intercellular layer and the S3 layer of the secondary wall, causing borehole-type damage to the wood (Bari et al. 2015; Daniel 2016; Goodell et al. 2017). In addition, soft rot fungi are more active in moist environments, such as conditions with high preservative content and high moisture content and are characterized by soft rot with a soft and watery wood surface. Thus, there are obvious geographical distribution differences in ancient architecture timber (Blanchette 2000).

Other biological factors that can cause damage to the wooden structure of ancient buildings are wood-boring beetles, termites, and other pests that live in cavities in the building wood and feed on the organic matter in the wood. They can also affect the strength and load-bearing capacity of construction elements. Due to the specificity of the environment in which the historical wood is located and the complexity of the cell wall degradation process, research is still needed on the decay and damage mechanisms of ancient architecture and its cell wall structural information and chemical composition.
(Dong 2017). On this basis, an in-depth understanding of wood degradation resistance and conservation methods for reuse may be significant for achieving sustainable building materials in the future.

**Fig. 3.** Historical wood biodegradation types: (A) white-rot, (B) brown-rot and (C) soft-rot (Fukasawa 2021). Reprinted with permission from John Wiley & Sons, Copyright 2021.

**Wood degradation forms of unearthed artifacts and its structure changes**

The burial environment of unearthed waterlogged wooden artifacts is a major factor in the degradation of wood, such as bacteria, fungi, aquatic animals, and substances including acids and alkalis. In a humid subsurface environment, waterlogged and anoxic conditions hinder the metabolism of fungi such as wood-decaying fungi, so wood destruction of waterlogged artifacts excavated in an anaerobic environment is primarily decomposed by bacterial microorganisms, while an oxygenated environment may promote soft rot fungal decay (Gjelstrup Björdal 2012; Dong 2017). Although the appearance and structure of the unearthed waterlogged wood may be preserved, its strength and structural integrity will suffer a great deal of damage with bacterial attack and chemical degradation. Owing to its degradation factors being limited by the environment, wood degrades more slowly under continuous bacterial attack and loses its mechanical strength relatively slowly (Klaassen 2008).

Wood-degrading bacteria have been identified including erosion bacteria, tunneling bacteria, and cavitation bacteria, with erosion bacteria being one of the most common types of bacterial degradation of waterlogged wood. In the early stage of erosion, mycelium enters the secondary wall from wood tissues such as ducts, degrades cellulose and hemicellulose in the cell wall in turn, and leaves characteristic erosion grooves in the inner cavity of the cell wall, while areas such as the lignin-rich intercellular layer are relatively well preserved (Pedersen et al. 2013; Lukowsky et al. 2018). Since cellulose and hemicellulose are less resistant to hydrolysis than lignin in an acidic condition (Holt and Jones 1983; Sandak et al. 2010), lignin and the intercellular layer are almost unaffected even in the later stages of decay when the secondary wall is completely degraded. Therefore, most of the ancient wood components degraded by erosion bacteria are mainly lignin, and only S1 and S3 layers are basically left in the secondary walls after degradation (Holt and Jones 1983; Pedersen et al. 2014). The decrease in crystallinity of cellulose after its structure change further leads to a significant destruction of the mechanical properties and mechanical strength of the unearthed wooden artifacts (Inagaki et al. 2010). Meanwhile, due to their tolerance of low oxygen conditions, erosion bacteria can even degrade wood buried deep in sediments, and although degradation is slow, it remains active for several years (Björdal et al. 2000). In some oxygenated environments, tunneling
bacteria and cavitation bacteria are also the main cause of historical wood degradation (Björdal et al. 1999; Pedersen et al. 2013; Pedersen et al. 2015). Tunneling bacteria can penetrate the intercellular layer of coniferous wood and the lignin-rich edge, partially degrading lignin while preferentially degrading cellulose components in the cell wall, causing the wood to soften and deepen in color (Pedersen et al. 2015). In contrast, cavitation bacteria usually penetrate the S3 layer, break down polysaccharides such as cellulose in the secondary wall and form prismatic and irregular cavities (Blanchette 2000; Pournou 2020).

**Wood degradation forms of ancient ship and its structure changes**

Wooden artifacts out of deep-sea waters and marine lakes are mainly ancient ship wood. Their destruction in low oxygen environments is caused mainly by erosion bacteria, but there are few studies on underwater wood bacterial degradation forms and their structural changes. Li et al. (2018) examined the ancient shipwreck of Song Dynasty “Nanhai I” and found that the internal aerobic and anaerobic bacteria, such as the Cytophagaceae-Flavobacterium (CF) group, were abundant and had a high capacity to degrade cellulose. The deposition of iron and sulfur compounds (especially pyrite, FeS₂) in ancient ship timbers, caused by iron and sulfur elements in the marine environment, caused great damage to wood cellulose and hemicellulose. For example, the ancient wood of the Vasa shipwreck contained a large amount of sulfuric acid generated from reduced and oxidized sulfur, and the Fenton reaction triggered by Fe²⁺/Fe³⁺ severely damaged the wood and organic matter such as PEG used for filling and consolidation, resulting in the destruction and degradation of the hull that has not stopped since the sinking (Shen et al. 2013).

In sum, moisture, oxygen, microorganisms, metal ions, and pH in the environment are the main factors that contribute to the degradation of ancient architecture, unearthed artifacts, and ancient ship timbers. Therefore, the environmental parameters of the historical wood, the form of damage and its structural changes are important clues for post-treatment solutions such as dewatering and consolidation and preservation (Dong 2017).

**Conservation Strategy**

Considering the special nature of historical relics, the consolidation and conservation of historical wood should be carried out under the premise of “not changing the original state of relics and repairing the old as the old”. Then, consolidation materials that are stable, resistant to aging and compatible with wood are used to give the wood long-term stable mechanical strength while minimizing damage to the wooden artifacts. The most critical thing is to meet the reversibility of future treatments (Han 2020).

The principle of wood conservation is essentially a technique that uses physical or chemical methods to modify the cellular properties of wood (S. 2006) (the involved cell modification methods are shown in Fig. 4) to improve the dimensional stability, mechanical properties, resistance to biodegradation, and other properties of historical wood. This results in the sustainable conservation of historical wood, such as ancient architecture and historical relics, and is usually classified as wood surface and cell wall modification, cell cavity filling, or a combination of both (Xie et al. 2013). Cell wall modification is the further formation of chemical bonds to enhance wood properties via reaction with chemical reinforcing reagents (reactive low molecular weight monomers or oligomers), or high temperature heat treatment, etc. It can achieve multi-dimensional directional reaction of the cell wall and multi-effects of one agent, such as improving the
dimensional stability and weathering resistance of historical wood (Mantanis 2017). Cell cavity filling uses the multi-scale pore structure of wood and the large number of hydroxyl groups to infuse chemical reinforcement reagents into the wood. The reagents deposited in the cell cavities polymerize under certain conditions, while the active functional groups of the reagents react with some wood components. In turn, it fills and plugs the cell gap, increases the density of wood cell tissue, significantly improves the mechanical properties of wood, and plays a good reinforcing effect (Xie et al. 2012; Laine et al. 2016; Qiu et al. 2018). The reagent filling and surface adhesion can reduce the entry of water into the cell wall, as well as form a protective barrier for the wood to prevent external damage factors, thus improving the hydrophobic, decay and aging resistance of the wood (Wang et al. 2020).

Fig. 4. Principles and methods of wood conservation and functional improvement (Wu 2021). Reprinted with permission, Copyright 2021, Journal of Central South University of Forestry & Technology.

In addition to the aforementioned methods of reinforcing and protecting at the wood cell level, in practice, preservation methods and purpose vary depending on the environment in which the wood is located and the structural damage factors. For ancient buildings, it is essential to be able to withstand various outdoor environments and biological attacks. Thus, the consolidation of wood in ancient architecture tends to use nondestructive monitoring, mechanical property assessment, species identification, structural repair, decay protection, and other measures to in-situ reinforcement treatment. Based on controlling their moisture content, preservatives such as oil-borne, water-borne, and organic solvent-borne are usually used to intentionally increase the decay resistance and insect/bacteria resistance of wood. However, these traditional preservatives contain
large amounts of heavy metals (such as copper, chromium, arsenic, CCA) and organic reagents, leaving a significant impact on the environment and have been banned in many countries (Jones et al. 2019). It is worth noting that studies have found that natural biomass extracts such as wood have some insect and microbial resistance, promising a biodegradable wood preservative (González-Laredo et al. 2015; Salem et al. 2016).

In contrast, excavated wooden artifacts and submerged ships often need to be transported to museums, laboratories, and other indoor locations for processing, conservation, and even public display. Their wood structure and chemical components changed during long periods of burial, usually containing high moisture content and accompanied by deterioration of basic density, mechanical properties and other characteristics are extremely detrimental to the salvage, conservation, and consolidation of historical wood. To extend the life of wooden artifacts, they require physical protection through timely shaping and dehydration during excavation in the field (Ma 2006; Shen et al. 2013; Ma 2020; Xu et al. 2020). For example, for “Nanhai I” ancient ship excavation and other such cases, many historical woods have been extremely fragile. Accordingly, Ma (2020) proposed a plastic mesh pocket device method, bandage sponge consolidation method, film pallet consolidation method, filler consolidation method and caisson consolidation method and other five external protection methods to prevent further damage to cultural relics, and for the subsequent desalination and dehydration, consolidation and repair work ready.

Such ancient wood is facing the main problem of dehydration and drying treatment, because it has a high moisture content, the rapid evaporation of water in the dehydration process will make the ancient wood cell walls subject to surface tension and collapse. This will lead to wood cracking and deformation, and this process is mostly irreversible, which easily cause incalculable losses to cultural relics (Hunt 2012; Babiński et al. 2014). The temperature, humidity and pressure can be controlled in such a way as to alleviate the dry shrinkage and wet expansion of wood, and to eliminate the existing sources of corrosion by destroying the living conditions of fungi, insects, and other biological organisms, in order to achieve conditions suitable for the preservation of historical wood. For example, the commonly used physical dehydration drying methods mainly include natural drying, freeze drying and supercritical fluid drying, etc., as shown in Table 1.

Taken together, freeze-drying has a hugely positive effect on the conservation of wooden relics, and the effect of this treatment on deep underground/submerged wood with high moisture content is also very impressive. In addition, air-cooled dehydration can significantly reduce the rate of water volatilization and overcome the effect of water surface tension, thus having a protective effect on the fragile cell walls.
Table 1. Physical Dehydration Protection Methods

<table>
<thead>
<tr>
<th>Dehydration and Drying Method</th>
<th>Processing mode</th>
<th>Advantages</th>
<th>Disadvantages</th>
<th>Reference</th>
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<tbody>
<tr>
<td>Natural drying</td>
<td>Place wood in a specific, stable environment to allow moisture to evaporate slowly and evenly</td>
<td>Smooth quality variation, good retention of the original color and texture of the wood</td>
<td>Long processing cycle, only for good quality ancient wood</td>
<td>(Liu 2015)</td>
</tr>
<tr>
<td>Freeze drying</td>
<td>Direct sublimation of moisture in the wood to water vapor by freezing at low temperatures</td>
<td>Avoids the effect of the surface tension, resulting in treated wood with good texture, dimensional stability, and low moisture absorption</td>
<td>The wood needs to be dried with the aid of chemicals such as polyethylene glycol to avoid freezing and cracking, and the equipment costs are high</td>
<td>(Grattan and McCawley 1978; Christensen et al. 2006; Lu et al. 2020)</td>
</tr>
<tr>
<td>Supercritical fluid drying</td>
<td>Taking advantage of the fact that gases cannot be liquefied above a critical temperature, no matter how much pressure is applied, the liquid inside the water-filled artefact is controlled above the critical point so that the gas/liquid interface disappears and drying takes place without surface tension in the liquid phase</td>
<td>Eliminates drying stress, shortens drying time, improve efficiency, yields appearance closer to inherent color, sterilization and drying can be completed simultaneously</td>
<td>Small equipment volume, high cost</td>
<td>(Cretté et al. 2013; Mu et al. 2020; Guo et al. 2022)</td>
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Zhang and Hu (2018) have used the air-cooled drying method to dewater and consolidate waterlogged wooden cultural relics with saturated absolute water capacity of up to 1,200%, with strong dimensional stabilization and while completely retaining the wood fiber cells intact. The method is also applicable to wood artefacts with a high degree of degradation. This is expected to resolve the volume limitations associated with freeze-drying and be applied to the conservation of large-scale waterlogged wooden relics. These methods eliminate the risks associated with chemical reagents to wooden relics without the addition of new materials, but their application is limited, so developing a green and reversible way of dehydrating and drying wood without altering its formation remains the goal of future research.

TRADITIONAL CONSOLIDATION AND CONSERVATION MATERIALS

The science of conservation has been a unique field of study for over a century. For unearthed relics with eroded properties and structure integrity, it is necessary to stabilize and protect the wood from further damage by biological organisms so that it retains its mechanical strength. In the future, it may be possible to enhance the performance of fast-growing timber for use in advanced applications such as construction, maximizing the efficiency of wood resource use and achieving sustainable development.

There are numerous methods and materials used for wood consolidation, including filling, impregnation, and in-situ polymerization (Broda and Hill 2021), but these consolidation methods have subsequently led to unanticipated problems. For example, alum, a commonly used reinforcing agent in the past, has caused extreme degradation of wood; polyethylene glycol (PEG) is widely used because it is relatively stable, reversible and inexpensive, but it causes the surface of wood to become dark and corrosive to metal (Gregory et al. 2012). When wood is impregnated with melamine-formaldehyde resin, the three-dimensional structure of the polymer formed is tightly bound to the wood cells, providing improved mechanical properties of the wood, while at the same time making the process irreversible (Devallencourt et al. 2000; Saiter et al. 2000; Spinella et al. 2021). Due to the specificity of the consolidation object, the consolidation material should be able to protect the appearance and dimensional stability of historical buildings and unearthed artifacts. What is more important is the compatibility with the wood structure and the reversibility of the treatment. History has taught us that it is difficult to date to have a method for the permanent preservation of a cultural object, even if that method is well suited to the circumstances. The choice of material and its impact is crucial for the long-lasting protection of the wood and must take into account the possible future re-treatment and protection it will face. If future studies reveal major problems with wooden artifacts treated with this material, the reversibility of the treatment will allow the removal of this restoration material to facilitate more optimal solutions. To preserve wooden cultural heritage effectively in the long run, it is necessary to look back at the past and propose novel consolidation materials and conservation methods based on the abandonment of traditional material defects.

Waxes, Oils, and Resins

Waxes, vegetable oils, and natural resins have long been used to reinforce and protect wood products (Unger et al. 2001). They are used to fill cracks in decayed wood and to reduce moisture absorption to reduce bio-erosion, thus improving the mechanical
stability and durability of wood (Schönemann et al. 2008).

The initial use of waxes or resins as consolidants was based on their impregnation in the molten state, with beeswax and paraffin being the more common. In addition to meeting the basic properties of moisture resistance and stability, wax-treated wood also reduces outdoor environmental effects such as weathering erosion and light degradation (Lesar et al. 2011). Scholz et al. (2012) experimentally modified wood with wax impregnation to demonstrate that this method can significantly reduce the water absorption of wood, while enhancing the structure of wood degraded by the modification and restoring some of the strength loss. Further, Akcay (2020) found that beeswax impregnation of wood resulted in significant filling of its cell cavities, which not only gave the wood water resistance, but also fungal durability and partial larval resistance. However, this treatment also has certain negative effects on the wood, such as in the case of severely decayed specimens, leading to a darker, more brittle wood. Related scholars hope to overcome this shortcoming of wax treatment by various combinations of wax and other materials, among which beeswax in KOH or NaOH environment has the possibility to reduce viscosity. However, the diffusion inside the wood remains slow, causing it to act mainly on the surface treatment (Schönemann et al. 2008).

In the search for consolidation materials with better permeability, vegetable oils are coming to the fore. Linseed oil has good gloss and abrasion resistance and is often used as a surface protection coating. However, due to its semi-dry nature, the drying time of linseed oil is several months, and it tends to cause structural softening of the wood in a humid environment. Tung oil, as a dry oil, becomes its substitute. Tung oil has thousands of years of history in China, and at the same time, China is also the first country to use tung oil to protect wood. It has become widely used in the field of ancient architecture and cultural relics consolidation and conservation. Due to the presence of a large number of conjugated and highly unsaturated bonds, α-eleostearic acid is more reactive with air. Arminger et al. (2020) found that tung oil can also quickly impart hydrophobicity to wood without drying equipment, thus providing good protection. Water resistance is still excellent even after the wood has been severely damaged. Similar to other oils, the high viscosity of tung oil is usually achieved by vacuum pressurization to improve its permeability in the wood (Žlahtič et al. 2017); however, problems such as non-uniform film structure caused by rapid drying may have some effect on its mechanical properties. Moreover, resins such as rosin have corresponding practical significance for wood consolidation, as a natural wood preservative that can sterilize and promote wound healing. Its hydrophobicity seals free hydroxyl groups in the wood, giving it the ability to resist moisture and thus improving durability (Li et al. 2011).

In conclusion, the advantages of such waxes, vegetable oils, and resins for wood consolidation are clear, improving the hydrophobicity and reducing the bioactivity of wood. Humar and Lesar (2013) treated Norway spruce and beech wood with linseed oil and tung oil, and the wood showed strong biological resistance to fungal decay such as brown rot and soft rot, with the effect of tung oil being more pronounced. Ahmed et al. (2020) and Hassan et al. (2020) showed that linseed oil has a high retention rate in wood treatment and resistance to termite attack and found that a mixture of a special heartwood extract and linseed oil could be used as an environmentally friendly wood preservative. With continuous research, these traditional reinforcement materials have been modified to obtain novel properties. For example, Janesch et al. (2020) used a mixture of tung oil and beeswax to deposit sodium chloride particles to create an entirely bio-based superhydrophobic coating to extend the service life of wood.
Alum

Alum (KAl(SO$_4$)$_2$·12H$_2$O), proposed by Herbst in the 1850s, was one of the first inorganic materials used for waterlogged antique wood reinforcement, often in combination with vegetable oil. Its effectiveness in the conservation treatment of unearthed waterlogged wooden artifacts was widely used at the time by museums around the world (Braovac and Kutzke 2012). The alum method of consolidation requires the impregnation of the decayed wood with its hot aqueous solution, which dries and crystallizes in the wood. This improves the mechanical properties and dimensional stability of the decayed wood and prevents the wood from shrinking.

However, alum contains sulfate, which is easily formed in moist wood during heat treatment, resulting in highly acidic alum-treated wood (pH: 1 to 2.5). It is capable of continuously degrading the remaining cellulose fibers and even lignin. Łucejko et al. (2021) investigated the current degree of degradation of some alum-treated wood products from the 19th and 20th centuries, and analytical pyrolysis (Py-GC/MS) tests showed that significant degradation and depolymerization of polysaccharide components such as cellulose occurred in all archaeological wood. Lignin was also highly oxidized in some samples. This study suggests that alum-reinforced wood is more susceptible to degradation than untreated wood. Research in museums in Norway, Sweden, and Denmark over the past two decades has shown that archaeological wood that has been consolidated using the alum method is extremely unstable (Lindahl et al. 2006), making this method of consolidating waterlogged wood no longer viable.

The alum method was in use for nearly 100 years until the 1950s, when polyethylene glycol began to be used as a substitute (Braovac and Kutzke 2012). Many famous artifacts were severely degraded and destroyed by alum treatment during this period, most notably the artifacts found at Oseberg, which are housed in the Viking Ship Museum in Norway. McQueen et al. (2017) concluded that not only were the alum-treated artifacts severely degraded, but that reprocessing them today presents complex challenges of alum removal and deacidification. In recent years, the application of non-aqueous alkaline nanoparticle dispersions has opened up possibilities for the protection of cellulosic substrates. The alkaline nanoparticle treatment of alum archeological wood by Andriulo et al. (2016) can effectively improve the acidic environment of the wood, giving hope for the restoration of alum-treated archeological wood.

Melamine-Formaldehyde Resin

An approach using melamine-formaldehyde resin (MF resin) was developed in the 1990s by the German Museum of Ancient Ships in Mainz for the consolidation of waterlogged wood, also known as the Kauramin method. It was introduced to replace the high formaldehyde content of the initially used polymer consolidation (Arigal C method) (Müller-Beck and Haas 1960; Wittköpper 1998; Wang et al. 2006).

MF resin treated antique wood preserves the original characteristics of the wood, such as age and workmanship, while forming polymers within the wood cells and binding tightly to them as its aqueous solution impregnates the wood. Although its distribution within the cells is not uniform, its own highly cross-linked three-dimensional network structure is an integral part of the wood tissue and forms a large number of hydrogen bonds (Saiter et al. 2000), contributing to the wood’s excellent mechanical properties and stability. Even severely degraded wood can be well protected, and the wood’s bioresistance is significantly improved (Devallencourt et al. 2000; Unger et al. 2001; Gindl and Gupta 2002; Spinella et al. 2021). Its consolidation mechanism is that first, water acts
as a carrier for the resin, and when it is adsorbed by cellulose, it sweeps away the resin that will remain in the microcavity, and then reactions such as hydrolysis, self-condensation or co-condensation occur depending on the temperature and pH of the consolidation. When relative humidity (RH) values are high, only water molecules can actually pass through the dense cellulosic portion of the substrate (Devallencourt et al. 2000).

MF resin consolidation has been shown to improve wood properties, e.g., Young's modulus and hardness of treated spruce were improved by 33% and 115%, respectively, compared to untreated wood (Gindl and Gupta 2002). Research on this method is still in progress and refinement. Spinella et al. (2021) studied MF resin reinforced archaeological wood for ten years and found that its mechanical effects and chemical interactions with the polymer inside the wood pores led to the irreversibility of the method. Kiliç and Kiliç (2019) noted that when reinforcing highly degraded wood with this resin, the impregnation process needs to be carefully followed and the pH and turbidity of the solution monitored. This is to improve the permeability of the resin and to avoid accumulation of cured polymers on the surface. In conclusion, although the melamine-formaldehyde resin process is irreversible, it has excellent curing properties and biological resistance to highly degraded and degraded waterlogged antique wood.

**Polyethylene Glycol**

Polyethylene glycol (PEG) is a polymer with repeating units (OCH₂CH₂) called polyethylene oxide/polyethylene oxide by the International Union of Pure and Applied Chemistry (IUPAC). Research on the use of PEG to reinforce historical wood was reported as early as the 1950s (Stamm 1956), and it is still a common material used in wood consolidation and preservation.

Polyethylene glycol is highly water soluble and can effectively replace the water in the wood cells to prevent collapse and deformation during drying. The consolidation microstructure mechanism is based on the part of the lumen filled with PEG to prevent water penetration to reduce water absorption, while the wood cell wall is smoother due to the swelling effect and PEG coverage, thus limiting the dimensional change (Meints et al. 2018; Jiang et al. 2021). PEG-reinforced wood has good stability. Glastrup et al. (2006) studied the distribution and aging of the Swedish Vasa, an antique ship treated with PEG in the 1960s, and showed that the PEG was still in fairly good condition after 30 years, with a molecular weight distribution similar to that of fresh PEG and few degradation products. Due to the high solubility of PEG, as well as the fact that the diffusion speed is not as fast as that of water molecules, there is a possibility of osmotic shock during the impregnation process, leading to cell rupture and wood damage, so the concentration gradient is usually set to gradually increase the concentration to prevent cell damage (Hoffmann 2013). In terms of penetration depth, the hygroscopicity of PEG varies with molecular weight, so a two-step impregnation of wood is recommended, i.e. low molecular weight PEG (PEG200-1000) has a high retention rate in wood and is commonly used to penetrate deep into wood to improve its dimensional stability. Meanwhile, high-molecular-weight PEG has low moisture absorption and can be used for surface treatment of wood with high degradation level (Bjurhager et al. 2012; Fejfer et al. 2020). In addition, polyethylene glycol is highly hydrophilic and is easily lost in a humid environment, causing a reduction in wood density and stability. For this reason, Yang et al. (2002) found that retreating polyethylene glycol-impregnated wood with isocyanate can effectively reduce reagent loss.
In general, polyethylene glycol is stable in nature, does not deteriorate with long-term storage, and is an effective material for dewatering and reinforcing waterlogged wood, and the use of polyethylene glycol is being gradually improved today. For example, red pine cell wall diffusion experiments showed that vacuum/pressure treatment could improve PEG impregnation efficiency and permeability (Jeremic et al. 2008). The constructed polyacrylic acid/polyethylene glycol semi-interpenetrating polymer network (PAA/PEG SIPN) can further improve the dry shrinkage and wet swelling properties of wood and the chemical resistance to loss, while improving the corrosion resistance, providing a novel idea for wood conservation (Liu et al. 2016). Soaking with buffer solutions such as oxalic acid (KH$_3$(C$_2$O$_4$)$_2$·2H$_2$O), ethylenediaminetetraacetic diamine (EDTA), and polyvinylpyrrolidone (PVP) prior to PEG treatment can effectively inhibit the deepening of wood color after consolidation (Qin et al. 2018).

Sugar

Since the beginning of the 20th century, sugars have been used in wood preservation to protect wood from decay and to improve stability and mechanical strength. The mechanism is to penetrate the wood with a highly concentrated solution prior to controlled drying, which causes the sugar to crystallize in situ. Because of its low price, non-toxic and non-corrosive, and compatible with the pores of wood, it can also be used for waterlogged wooden relics (Morgós et al. 2015).

Sucrose was the first sugar used to consolidate water-saturated wood, effectively penetrating the wood tissue to crystallize within the cells and potentially interacting with other polymeric hydroxyl groups such as cellulose to strengthen the cell walls (Parrent 1985). However, this sugar will hydrolyze over time, and long-term use of sucrose will cause white crystals or brown sticky films to appear on the surface of the wood, making them difficult to remove and detracting from the aesthetics. The expansion and contraction of crystalline deposits exuded under high humidity conditions also poses a risk of damage to untreated wood (Parrent 1985; Kennedy and Pennington 2014; Morgós et al. 2015). Meanwhile, its own hygroscopic, wood treatment in the environment after the change of instability and prone to microbial erosion, and then fermentation lost protective effect.

One way to avoid such problems is to use inactive sugars that cannot be hydrolyzed, such as sucralose and trehalose, which are structurally similar to sucrose and are relatively inactive and have some long-term stability (Schebor et al. 1999; Richards et al. 2002). In Kennedy et al.’s experiments with the same concentration (60%) of sucralose and trehalose impregnated with degraded birch tongue depressor, their anti-shrinkage rates (ASE) after air drying were 63.2% and 61.8%, respectively. Both were higher than 59.0% for sucrose, demonstrating its good performance at low concentrations. However, some warping and deformation was observed in one of the sucralose-treated samples, indicating that the high stability of sucralose also limits the reactivity of the reaction with wood polymerization. The Young’s modulus and fracture stress of sucralose and trehalose-reinforced waterlogged wood (29.0 GPa/232.8 MPa, and 36.9 GPa/260.6 MPa, respectively) were much higher than those of sucrose and fresh wood (19.1 GPa/196.9 MPa, and 11.5 GPa/135.5 MPa, respectively) (Kennedy and Pennington 2014; Tahira et al. 2017). Trehalose is a disaccharide that still works well even at low concentrations and has a long-lasting stabilizing effect. In Nguyen and Liu’s experiments on the consolidation of ancient wood, the shrinkage of the cross-section of trehalose-treated wood was less than 2% and the hygroscopicity was about 3.9 to 4.9%. It is lower than 6.9 to 7.5% of untreated wood (Nguyen et al. 2018; Liu et al. 2019). Compared to sucrose and sucralose, trehalose...
treatment is fast, inexpensive, safe, fully reversible, and can be applied to severely damaged wood, making it a viable consolidation method for waterlogged wood (Kennedy and Pennington 2014; Morgós et al. 2015). But sucralose has been shown to have a potential antibacterial effect in certain circumstances and may be more effective in protecting unearthed wood (Omran et al. 2013).

Research on sugar alcohols such as lactitol, mannitol, sorbitol, etc. is also in progress, and various sugars have their own properties and advantages, such as lactitol is more resistant to high temperature and alkaline conditions and has higher biological resistance (Morgós et al. 2015); sorbitol is more effective than alginate at low concentrations and more cost-effective, etc. (Jones et al. 2009). Although there are currently successful cases of sugar consolidation, it cannot be ruled out that it may improve wood properties by forming a crystalline sugar lattice in the internal pores of the wood. Therefore, much research is needed in the future to investigate the long-term stability and reactivity of these substances. In an uncontrolled wood environment, the introduction of large amounts of sugars carries the risk of further damage to the wood through biological attack by bacteria, fungi, insects, etc.

**Acrylic and Epoxy Resins**

Since the 1960s, polymer materials have been widely used in wood and heritage conservation, with acrylic and epoxy resins being the most studied fossil-based monomers. Acrylic resin (Paraloid B-72) is an organic soluble copolymer consisting of 34% ethyl methacrylate and 66% methyl acrylate. Its colorless and transparent, good thermoplasticity, and high tensile strength and elongation have favored its use as a consolidant, binder, and sealing protective agent for the conservation of cultural relics, etc. (Carretti and Dei 2004; Kotlík et al. 2014), and acetone, toluene and ethyl acetate are often used as its reinforcing solutions to treat wood (Traistaru et al. 2011). Epoxy resin is a thermosetting resin made of polyepoxide cross-linked with phenol and polyol, which has the advantages of high bond strength, low toxicity and low cost, and has been used in the field of historic preservation since the 1960s and 1970s (Wang et al. 2017).

Acrylic resin consolidation methods are based on its excellent thermal stability, as well as its good film formation, hydrophobicity, adhesion, and some reprocess-ability. Wood is usually protected by total impregnation with a concentration gradient or by spot, drip, or spray application (Gong et al. 2022). Mankowski and Andres (2015) vacuum-impregnated fungus-infested wood with B-72 and showed a significant increase in both wood density and down-grain compressive strength, demonstrating the effectiveness of acrylic resin in strengthening historical wood. Wood treated with acrylic resin basically meets the guideline of “no change in the original state of the artifact” under certain process conditions, and it has superior heat aging stability, but the molecular structure will change during the light aging process (Li et al. 2017). Cocca et al. (2004) found that the properties of acrylic resins degrade under the influence of temperature and UV light, and their physicochemical properties are damaged. Using NMR and FTIR studies, Favaro et al. (2006) found that the acidic groups formed during the aging process further accelerate wood erosion. In general, thermal aging and light aging resistance are important factors in the long-term stability of the material. To improve the performance of acrylic resins, treated spruce with acrylic resins containing UV absorbers under weathering conditions showed a significant reduction in wood surface degradation (Ozgenc and Yildiz 2016). Current research on absorbents such as surface-treated nano-TiO₂ (Veronovski et al. 2013) and small amounts of fluorinated monomers (Bongiovanni et al. 2002) provide the technical
basis for long-term outdoor protection of acrylic resin-treated wood.

Epoxy resin has high bonding strength and is compatible with wood, so it is often used to reinforce and bond large wooden structures in ancient architecture, such as the repair of weathered, broken, de-tenoned and split wooden elements in Nanzen Temple in Shanxi with epoxy resin (Zha 2018), and the restoration of ancient architectural heritage in Brazil and Spain (da Silva Bertolini et al. 2013; Vilches Casals et al. 2013). All of them confirmed the feasibility of epoxy consolidation of large wooden elements, which is not only simple, but also preserves the original structure and appearance of ancient architecture, while effectively improving the load-bearing capacity of wooden structures. However, epoxy polymers are sensitive to ultraviolet light, and photodegradation will result in changes in color and physical properties. Overall, the greatest advantage of the epoxy is in-situ restoration with little damage to large wooden structures such as historic buildings, but it has to be acknowledged that this method is irreversible and therefore rarely used on wooden artifacts.

NOVEL CONSOLIDATION/CONSERVATION MATERIALS AND PROSPECTS

Biomass Materials

The materials used in biomass materials are mostly derived from natural materials such as animal feathers, shells, microorganisms or plants, and use biomass cellulose, animal proteins and other material components to strengthen historical wood. Many bio-based adhesives and fillers may lack resistance to biological decay, limiting their use to wooden artifacts preserved indoors, rather than items that require in situ treatment outdoors, such as architectural wood structures.

Keratin and oligoamides

Proteins, molecules that provide structure in biological cells, are potentially valuable for reinforcing degraded wood, and thus proteins as wood consolidation materials have been investigated. Keratins are the most abundant biopolymers on earth, second only to cellulose and chitin (Yutaka et al. 2002; Kawahara et al. 2004; Lange et al. 2016). As a fibrous structural protein, keratin exists in the epidermis, hair, nails, and horns of vertebrates. It is highly resistant and biologically active to acidic media and tolerant to microbial attack and has the basic conditions to conserve wood. However, keratin is insoluble in water and organic solvents, so it needs to be hydrolyzed before reinforcing the wood, usually using NaOH (Endo et al. 2008; McKittrick et al. 2012).

The mechanism of keratin reinforced wood is different from the way polyethylene glycol, alginate, and other materials fill wood cell cavities, because it has a density similar to that of cell wall material (ca. 1569 kg/m³). It is small enough to diffuse rapidly into wood tissue and penetrate cell walls, adhering to the intermediate lamellae and thus reinforcing the cell wall structure (Yutaka et al. 2002; Endo et al. 2010; Jensen et al. 2012; Nguyen et al. 2018). Endo et al. (2010) tested the physical and mechanical properties of hydrolyzed keratin impregnated wood and showed that keratin treatment restored the mechanical properties; there was a good correlation between modulus of rupture (MOR), modulus of elasticity (MOE), and anisotropy of waterlogged ancient wood, effectively strengthening the wood cell walls. Kawahara et al. (2004) and Fejfer et al. (2015) showed significant differences in molecular weight between α-keratins (mainly from wool, etc.) and β-keratins (mainly from feathers or down, etc.), which resulted in variation of penetration and
consolidation (molar mass of feather keratins < 10 kDa, molar mass of wool keratins 25 to 30 kDa), with feather keratins penetrating the cell wall and having greater resistance to dry shrinkage (ASE). Thus, feather keratin treated wood has better dimensional stability. The antimicrobial activity of keratin-treated wood provided long-term stability by protecting the wood from micro-organisms such as bacteria and fungi, while retaining its basic color characteristics; and improved its resistance to UV light (Yutaka et al. 2002; Endo et al. 2010; Nguyen et al. 2018). However, the large amount of salt produced during hydrolysis preparation results in keratin-treated wood being more hygroscopic, reducing rapid water loss during drying, but also increasing the risk of wood product breakage in humid environments (Kawahara et al. 2004; Endo et al. 2010). The ability of keratin to penetrate cell walls leads to increased dimensional and mechanical stability and is a promising consolidation material for the protection of waterlogged wood products. Many uncertainties require further study to improve the performance and value of keratin-treated wood.

Oligoamides and other polymers prepared from natural polymer compounds have good permeability and compatibility due to their water solubility and low molecular weight, providing more references for future novel consolidation materials. For example, Cipriani et al. (2013) have synthesized polyethylene-L-tartaramide, polyethylene-D(+)-glucaramide, poly-ethylene-α,α-trehaluronamide and three other hydroxylated oligomers from derivatives of natural compounds (Fig. 5).

![Fig. 5. Synthesis of hydroxylated oligoamides: (A) polyethylene-L-tartaramide, (B) polyethylene-D(+)-glucaramide, and (C) polyethylene-α,α-trehaluronamide. Reprinted from Cipriani et al. (2013) with permission from John Wiley and Sons, Copyright 2013.](image-url)
These new water-soluble oligomers have a high affinity for lignin, and effectively stabilize the wood and reduce its shrinkage (39 to 49% shrinkage). The permeability and reversibility of these oligomers have been demonstrated using historical wood impregnation and FT-IR analysis. These attributes of great importance in the development of new reinforcement products.

**Chitosan and guar gum**

Chitosan is a renewable and non-toxic N-deacetylated derivative of the natural polysaccharide chitin. Its structure is similar to that of wood cellulose. It is a chain-like macromolecule formed by the condensation of glycosyl groups. Chitosan can easily penetrate the pores of wood fibers due to its good compatibility with the same substances, and is more biocompatible and biodegradable than synthetic polymers (Xia 2013; Christensen et al. 2015; Walsh et al. 2017). Its fungal resistance and metal chelating properties have been proven in studies; thus, chitosan is a very promising material for consolidating and conserving historical wood (Ravi Kumar 2000; Broda 2020). Besides, an extracellular polysaccharide guar gum consisting of galactose and mannose also shows good penetration of and compatibility with waterlogged ancient wood, with strong consolidation properties even at concentrations as low as 1% (Walsh et al. 2017).

Christensen et al. (2015) used 2% acetic acid solution of chitosan to reinforce waterlogged ancient wood from the Viking Age (>1,000 years ago). High-performance liquid chromatography (HPLC) showed that the chitosan solution penetrated more than 1 cm along the grain of the wood, and even heavily degraded wood regained some of its mechanical strength. This indicates that chitosan in low concentration solution can penetrate wood without altering its state and that the open structure of wood offers the possibility of further protection while reinforcing it. Wakefield et al. (2018, 2020) tested the reinforcing properties of chitosan at different levels of polymerization and deacetylation and its tert-butyldimethylsilane derivative (TBDMS-chitosan, Fig. 6 Aa) on dry degradation of ancient wood. TBDMS-chitosan completely penetrated the wood and covered the cell walls rather than filling them (Fig. 6 Ab), indicating that the wood could be re-treated in the future, if necessary, without the need to remove TBDMS-chitosan, which is expected to be applied to future re-conservation of alum-treated wood products.

**Cellulose and its derivatives**

Cellulose, a natural linear polysaccharide consisting of glucosyl units linked via β-1,4-glycosidic bonds, is the most abundant and renewable organic polymer material on Earth. It is also one of the main components of the wood cell wall, providing strength to the cell wall. The hydrogen bond network of cellulose prevents melting and dissolution in many solvents, making it stable (Eichhorn et al. 2010). It is a viable and promising material for wood consolidation.

Cipriani et al. (2010) was one of the earliest to start using modified cellulose as a wood consolidation material. After an accurate study of the degradation process of waterlogged wood products, cross-linkable cellulose ethers such as allyl cellulose, allyl carboxymethyl cellulose, and allyl n-hydroxypropyl cellulose were prepared to reinforce wood. FTIR showed that cellulose ethers have a high affinity for lignin (lignin is the main structural component of more degraded wood (Colombini et al. 2009)) and some degree of permeability, and are feasible as a wood consolidation material, but the cross-linking reaction of allyl ethers resulted in low treatment reversibility. Among them, carboxymethyl
cellulose (CMC) and hydroxypropyl cellulose (HPC) are common cellulose derivatives used in wood processing and have strong biocompatibility and diverse properties depending on the functional groups introduced. Fulcher (2017) has studied the ability of cellulose-based consolidation materials such as HPC to meet most criteria for reversibility, dimensional stability, wood compatibility and non-toxicity, but it is more difficult for cellulose-based consolidation materials to fully penetrate waterlogged wood and their performance still requires further considerable research and optimization. In addition, cellulose can be used as filler to improve the comprehensive performance of the composite. For example, the mechanical properties of ancient wood such as stiffness and flexural strength were greatly improved after the composite microcrystalline cellulose/Paraloid B-72 consolidation. The radial and tangential surface hardness is almost equal to that of fresh wood (Cataldi et al. 2015).

Recently, Wakefield et al. (2020) synthesized two natural cellulose derivatives: 6-deoxy-6-(ω-aminoethyl) aminocellulose (AEA-1) and its alkyl derivative 6-deoxy-6-(ω-hydroxyethyl) aminocellulose (HEA-1). Most of these aminocelluloses are water soluble and have excellent film forming properties. In ultracentrifuge analysis, the results of matrix-free sedimentation velocity technology and sedimentation equilibrium technology showed that their monomer molar masses (4.5kDa and 5.5kDa, respectively) were within the range suitable for use in archaeological wood (Wakefield et al. 2018), and both showed protein-like self-binding behavior and partial reversibility. Among them, AEA-1 showed complete reversibility up to 12 kDa. In principle, this means that based on effective penetration and increased wood strength and stability, polymers can be removed from wood if necessary in the future. This has far-reaching implications for future research into materials for archaeological wood reinforcement treatments.

Lignin and its derivatives

Lignin consists of cross-linked phenolic precursors and is the second largest natural polymer after cellulose. It also serves as one of the major components of the wood cell wall, providing structural rigidity to the wood cells. Due to its high chemical and biological resistance, it is usually the main residual material of unearthed wood, so it is of research value to explore lignin-based consolidation materials (Colombini et al. 2009).

Because lignin itself is large and difficult to penetrate uniformly when impregnating wood, McHale et al. (2016) completely and uniformly penetrated 1 cm³ of waterlogged archaeological wood samples with lignin-like oligomers (dehydrogenated polymers, DHPs) synthesized from isoeugenol in 10% ethyl acetate solution. SEM did not observe any impregnated material, indicating that the cell walls would be covered after drying. The tests demonstrated the effectiveness of the dehydrogenated polymer as a wood consolidation material and showed that both DHP and ethyl acetate could be recovered. The in-situ polymerization of isoeugenol for wood consolidation has also been investigated, using horseradish peroxidase (HRP) and H₂O₂ to polymerize isoeugenol monomers in aqueous solution at room temperature to form lignin-like materials in situ. It forms a chemically stable β-5’ fraction within the wood, allowing the wood to be effectively reinforced. The SEM image also shows that this is not filled wood and that the open structure is retained (Fig. 6B), allowing for future reprocessing. However, its consolidation ability and long-term stability need to be further investigated, and it is expected to become a green consolidation material for waterlogged wood (McHale et al. 2017).

Lignin phenol, a lignin derivative extracted directly from wood, has a better effect on wood stability. Nagamatsu and Funaoka (2003) found that lignin-based polymers, lignin
phenols (LPs), were effective in preserving powdered material (e.g., cellulose) by applying heat and pressure, and this is the case with some dry archaeological woods. Currently, lignin phenols have been used for archaeological wood conservation and their performance is significantly better than that of PEG4000 (Kataoka et al. 2007). In addition, Salanti et al. (2016) prepared lignin-organosilicon hybrids with allylated lignin as crosslinker and solubilizer under Karstedt catalyst, and the hydrophobicity of wood samples increased after consolidation, but the required conditions and limitations were difficult to be widely applied to the treatment of waterlogged wood products. Antonelli et al. (2020) produced lignin nanoparticles (LNPs) from beech wood via a non-solvent dialysis method, and their permeability in the wood was 1 mm, as with CNC, and they did not achieve satisfactory consolidation (ASE of 51 to 88%). When using lignin nanoparticles for treatment, the lignin source wood that matches the color of the treated object needs to be considered. At present, the use of lignin in wood reinforcement still requires a lot of research to find suitable modified lignin-based materials or the use of polymers with lignin as filler to achieve the same dimensional changes in wood and consolidation materials with changes in relative humidity (Christensen et al. 2012).

![Figure 6](image.png)

**Fig. 6.** A (a) 3,6-Silylated chitosan, and SEM–EDS images taken from 1 cm cube of artificially decayed birch treated with TBDMS-chitosan (b) image showing the region used for elemental mapping, (c) EDS map of silicon (Wakefield et al. 2020); B SEM image of the centre of wood (McHale et al. 2017).

**Nanocomposites**

*Nanoparticles*

With some traditional consolidation materials (e.g., alum, polyethylene glycol, etc.) treated wood and the acidic environment created during its ageing process, further degradation of already damaged cellulose and other wood tissues present challenges for future wood consolidation and conservation. Alkaline nanoparticles (NPs) are a promising material for neutralizing the acidity of wood. Alkaline hydroxide and carbonate nanoparticles can react with acidic sulfides to form highly insoluble alkaline earth metal sulphates, iron carbonates or oxides, eliminating the possibility of sulfuric acid production (Schofield et al. 2011; Baglioni et al. 2015; Poggi et al. 2016; Schofield et al. 2016).
In wood deacidification experiments on the ancient ship Vasa, alkaline earth metal carbonate and hydroxide nanoparticles provided an alkaline reservoir within the wood, and the nanoparticles absorbed from the dispersion adhered to the wood walls, releasing hydroxyl ions to neutralize the wood (Giorgi et al. 2005, 2006). Aging studies on Vasa wood have shown that the nanoparticles are effective in protecting the wood from further acid degradation. Both Ca(OH)$_2$ and Mg(OH)$_2$ nanoparticles improved the pyrolysis resistance of Vasa pine and oak after treatment, with the maximum pyrolysis temperature returning to fresh wood values and the resulting alkaline reservoir providing continuous deacidification of the wood (Chelazzi et al. 2006). In terms of permeability, both magnesium and calcium nanoparticles can penetrate the wood structure to a depth of 1-2 cm or more. Mg(OH)$_2$ nanoparticles with an average size of 90 nm have better permeability than Ca(OH)$_2$ inside the wood, while the rate of cellulose photooxidation is reduced in the presence of the deacidification by-product MgCO$_3$ (Giorgi et al. 2005; Chelazzi et al. 2006; Giorgi et al. 2006).

Nevertheless, lignin and related compounds are more sensitive to alkaline media and there is a possibility of damage to the mechanical stability of the wood. Several researchers (Schofield et al. 2011; Chadwick et al. 2012; Schofield et al. 2015; Schofield et al. 2016) investigated alkaline earth metal carbonates such as BaCO$_3$, CaCO$_3$, and Cs$_2$CO$_3$, which are less alkaline, as deacidifying materials; these are common ores and can be easily processed into 20 to 50 nm nanoparticles. In tests on the woodwork of the Mary Rose, these nanoparticles catalyzed the conversion of iron oxide sulfides to soluble iron sulfates by forming insoluble sulfates that neutralized the acidity of the wood (Schofield et al. 2015). Ba and Cs carbonate nanoparticles exhibited their unique properties by X-ray absorption spectroscopy (XAS), energy dispersive X-ray scanning electron microscopy (SEM-EDS) and X-ray fluorescence analysis (XRF) in the experiment of Schofield et al. (2015) to provide an effective solution to cope with the short- and long-term hazards of acid degradation, and their related reaction principles are shown in Fig. 7. Cross sections of the treated samples showed complete penetration of the nanoparticles into the wood structure (Fig. 7A-c), most likely using open conduits for migration, and SEM-EDS also analyzed the sulfur content, indicating that SrCO$_3$ nanoparticles not only penetrated the wood, but that strontium reacted with the sulfide. However, it is more toxic than CaCO$_3$, and the additional precautions required to use BaCO$_3$ in practical protection programs make it less than ideal as a consolidation material (Schofield et al. 2011, 2015, 2016). Chadwick et al. (2012) found that SrCO$_3$ nanoparticles were very slow to penetrate the wood, taking a year or more. As a result, CaCO$_3$ nanoparticles place very little stress on the artifact material, cause minimal changes to the item during drying, and have a low environmental impact. It may be the ideal choice for the future widespread application of historical wood consolidation and conservation. Alkaline hydroxide and carbonate nanoparticles are not only suitable for the degradation of highly waterlogged historical wood artifacts but can also be used to address the primary problem of sulfuric acid degradation of natural heritage artifacts worldwide, providing a solution for the preservation of important historical wood products.

Nanocellulose

Cellulose-based materials and nanomaterials are increasingly being applied to biocomposites such as nanofillers, protective coatings and antimicrobial films, with the advantages of low density, good mechanical properties and low toxicity (Faruk et al. 2012; Lin et al. 2012). Nanocellulose is an ideal material for the preparation of novel
biopolymers. Cellulose nanocrystals (CNC), with an average diameter of 10 to 20 nm, are rod-shaped crystals with a high axial modulus of elasticity (Moon et al. 2011; Kim et al. 2015). Antonelli et al. (2020) compared the effect of bacterial nanocellulose and CNC consolidation and demonstrated that bacterial nanocellulose had better penetration than CNC (CNC only penetrated 1 mm into the wood) and was effective in stabilizing water-saturated broadleaf wood products (80 to 88% ASE), but the stability of old coniferous wood was not controlled. For this issue, the authors suggest exploiting the potential of nanoscale consolidants to penetrate the wood’s ultrastructure by modifying the shape of the nanocellulose or combining filamentous and spherical nanoparticles to obtain a network structure capable of filling the voids and supporting the cell walls for optimal results.

Cellulose can be used as a filler to improve composite properties, while nanomaterials are often used to enhance material-matrix interactions due to their size advantage. For example, the composite prepared by blending CNC with photocurable resin significantly improved the thermal stability and mechanical properties of the pristine matrix, demonstrating the effectiveness of CNC as a nanofiller (Cataldi et al. 2017). It can also contribute to the performance and functionality of wood, increasing its stability and biological durability. Basile et al. (2018) prepared eco-friendly and bio-inspired consolidants from CNC, lignin/siloxane derivatives (PDMS) mixture, and the hardness of decayed wood was substantially increased after treatment. Hamed and Hassan (2019) used hydroxypropylcellulose polymer (Klucel E) blended with varying concentrations of nanocellulose to investigate its performance as a wood strengthening material. The percentage of the mixture varied depending on the concentration of Klucel E. The maximum percentage of NC concentration was 10% and the results showed that the use of nanocellulose as an additive was effective in improving its penetration into the wood structure and the compressive strength of the reinforced wood without side effects on the wood after ageing. Additionally, recent studies have shown that the compressive strength of wood treated with 30% cellulose nanofibrils (CNFs)/Klucel E composites was increased by 34.38%, which is of great significance for wood consolidation applications (Younis et al. 2023).

Fig. 7. The penetration of SrCO$_3$ nanoparticles in timbers and the correlation of strontium and sulfate through the cross-section: (A) SEM micrograph of Mary Rose timbers after treatment with SrCO$_3$ (inset) EDS strontium content map of same area, (B) X-ray fluorescence image of the strontium distribution on the macroscale, (C) sulfur and strontium profile using EDS; (inset) line analysis throughout the cross-section. Reprinted from Schofield et al. (2011), Nanoparticle de-acidification of the Mary Rose, Materials Today 14(7), Copyright (2011) with permission from Elsevier.
Other polymers and composite systems

Organosilicon compounds have been used for wood protection since the second half of the 20th century. With the application of nanotechnology, Andriulo et al. (2017) developed a new organic/inorganic composite system consisting of propylene glycol-modified silanes and Ca(OH)₂ alkaline nanoparticles that can effectively penetrate wood structure and polymerize with lignin to form a three-dimensional polymeric network. While reinforcing the wood, it can also de-acidify and adjust the pH of wood. Broda et al. (2020) investigated a method of reinforcing waterlogged wood with organosilicon compounds of varying chemical compositions and molecular weights, and found that the low molecular weight organosilicons with high permeability and functional group chemicals that can interact with wood polymers to form stable coatings, typically have excellent reinforcing properties. For example, (3-mercaptopropyl) trimethoxysilane, (3-aminopropyl) triethoxysilane, and 1,3-bis(3-aminopropyl)-1,1,3,3-tetramethyldisiloxane yielded ASEs of 98%, 91% and 91% respectively, demonstrating the effectiveness of organosilicon compounds in reinforcing waterlogged wood. Among them, methyltrimethoxysilane (MTMS) treatment can also increase resistance to brown rot fungi (Broda 2018). In addition, experiments with treated wood in ethanol solutions have shown that the treatment with siloxane and amino silane is reversible, and wood impregnated with hydrophobic alkoxysilanes can be further reprocessed.

Halloysite is an aluminosilicate clay mineral (Al₂Si₂O₅(OH)₄). The bioactive substances and reverse charges on the inner and outer surfaces of nanotubes allow their selective modification by various substances and serve as nano-containers and carriers for the release of active molecules, which are ecologically sustainable and non-toxic (Lazzara et al. 2018; Zhang et al. 2019). Halloysite nanotubes (HNT) increase the thermal stability and mechanical properties of beeswax, thereby solving the problem that wax is difficult to penetrate wood due to its hydrophobicity and high molar mass and improving its mechanical properties. Cavallaro et al. (2015) treated sample timber from the ancient ship Chretienne C (second century BC) with HNT mixed with beeswax in acetone and the volume shrinkage of the reinforced timber was reduced to 6.2% form 40.6% without treatment, and the ASE was 85%. These findings verify the effectiveness of the HNT/beeswax composite system for strengthening antique timber.

Ca(OH)₂-loaded HNT as a nanofiller with antimicrobial activity is able to sustain long-term deacidification of wood samples. The Ca(OH)₂-HNT mixture was dispersed in PEG 1500, and a composite deacidifying consolidation material Ca(OH)₂-HNT/PEG suitable for waterlogged archaeological wood was proposed. This environmentally friendly method is of great significance for the conservation of cultural heritage, as it significantly increases the strength of wood and provides effective long-term effective protection for wood structures that have deteriorated under acidic conditions (Cavallaro et al. 2018). However, these treatments require acetone as an organic volatile solvent, which limits both their sustainability and the possibility of applying them to large shipwreck artefacts. Because of this, Lisuzzo et al. (2021) proposed a Pickering emulsion based on HNTs, using paraffin wax as the inner phase of the oil-in-water droplet. Impregnated wood tests showed that this organic/inorganic hybrid system effectively reduced the volume shrinkage of wood (87.5% ASE) and enhanced its mechanical properties without affecting its macroscopic surface. Notably, water was the only solvent used throughout the reinforcement process; therefore the method is highly biocompatible and ecologically sustainable. This represents an environmentally friendly method of protection of aged wood that may be extended to other materials.
Walsh et al. (2014) constructed a supramolecular polymer network of catechol and naphthol functionalized chitosan (PolyCatNap) based on guar gum and chitosan (Fig. 8A shows a schematic diagram of polymer network formation). The reinforcement of unearthed wooden relics resulted in increased structural stability and biological resistance, as well as the removal of Fe$^{3+}$ from the wood to prevent further acidification degradation. The microscopic and high-resolution FT-IR images are shown in Fig. 8B, indicating the characteristic signals of cellulose (1347 to 1400 cm$^{-1}$), and lignin (1486 to 1529 cm$^{-1}$) in treated and untreated wood and chitosan (1630 to 1690 cm$^{-1}$) in PolyCatNap treated samples, with low purple and high red in the high-low absorbance range. Fe$^{3+}$ deposition in the treated samples can also be effectively removed without destroying the wood. At present, this new supramolecular polymer network system treatment is effective for structural stability, biological resistance, and Fe$^{3+}$ removal, and is environmentally friendly and reversible. This has epoch-making implications for the conservation of wooden cultural relics and structures.

![Fig. 8. A: Schematic representation of the formation of the functional supramolecular polymer network; B: Treatment of Mary Rose timbers with PolyCatNap: (a) optical microscope (left) and images of integration over specific spectral regions (right) from high-resolution FT-IR imaging, (b) photographic images of the treatment with PolyCatNap and pure chitosan of a chisel handle found on board the Mary Rose with significant surface iron deposits over a period of 6wk, (Inset) with removal of the treatment to leave a cleaned artifact surface. Reprinted from Walsh et al. (2014) with permission from PNAS, Copyright 2014.](image)

**Green Bionic Materials and Polymerization Technologies**

To further explore green consolidation materials, bionics (i.e., nature-inspired materials) are ideal due to their unique layered (porous) structure, which can achieve properties such as high strength or high flexibility and good compatibility with wood (Christensen et al. 2012). For example, biomineralization has been used for artificial bone materials (Thackray et al. 2004) as well as highly durable non-organic “wood” (Shin and Exarhos 2007). Regarding the consolidation of waterlogged heritage wood, Li et al. (2022) constructed a skeleton-like topology combining a rigid exterior with an elastic interior by immersing PEI (poly(ethyleneimine)) molecules into the wood matrix and then spraying GA (glutaraldehyde) or BDDE (1,4-butanediol diglycidyl ether) solution onto the wood surface (Fig. 9 A). This structure effectively resists shrinkage stress, maintains excellent dimensional stability, and is environmentally friendly.
Atom transfer radical polymerization (ATRP) is a rapidly developing technology for living/controlled polymerization and has been used widely in the structural design of polymer molecules and the synthesis of multifunctional polymers. The polymer formed by ATRP can be grafted to cell walls to reduce brittleness caused by cellulose degradation during the consolidation process. The electron transfer re-generation activator ATRP (ARGET ATRP) method is proposed to continuously convert transition metal compounds from high to low valence by adding mild reducing agents to reduce the amount of transition metal catalyst in the reaction system. Wang Kai’s group (Zhou et al. 2019) from Peking University explored the use of ARGET ATRP to maintain the dimensional stability of waterlogged archaeological wood after drying, and the scheme is shown in Fig. 9B. The waterlogged archaeological wood samples (*Pinus massoniana*, maximum moisture content of ca. 529%) were modified with 2-bromoisoobutyryl bromide (**C**4**H**6**Br**2**O) in CH2Cl2 to obtain C-Br bonds as initiators, and treated in ethanol with CuBr2 (catalyst), ascorbic acid (reducing agent), and PMDETA (ligand) polymerized into the cell walls. The results showed strong dimensional stability of the treated wood (87.8% ASE for wood grafted with polystyrene and 98.5% ASE for wood grafted with polybutylmethacrylate). On this basis, the initiator functionalization method was improved, while an advanced thermal initiation ARGET ATRP system was proposed. The amino group in the waterlogged wood was functionalized with mercaptoethylamine (MEA) to realize penetration at room temperature and heating polymerization, and effective results were obtained. In addition, further experiments showed that the distribution of the polymer in the wood samples was related to the propagation rate of polymerization and the anti-shrinkage mechanism of the treated wood. It is possible that the expansion stresses generated during the surface-initiated ARGET ATRP process counteracted the shrinkage stresses during drying (Zhou et al. 2021; Zhou et al. 2022). In summary, the ARGET ATRP method has great potential for improving the dimensional stability of waterlogged wood and provides additional directions for possible future wood reprocessing.
Fig. 9. A (a) Schematic diagram showing dehydration/consolidation process of a waterlogged wood using the PEI/GA or PEI/BDDE combinations and the corresponding cross-linking reactions and hydrogen-bond interactions. Reprinted with permission from Li et al. (2022). Strong/stiff exterior and elastic interior: An effective biomimetic topological structure for the consolidation of waterlogged wooden archaeological relics during dehydration, *ACS Applied Polymer Materials* 4(11), Copyright (2022) American Chemical Society; B Scheme depicting the conceptual process of grafting polymer chains within wood cell wall using ARGET ATRP (Zhou et al. 2019).
CONCLUSIONS AND PERSPECTIVE

This review has focused on the structure of wood, its historical applications, and its forms of degradation damage and physicochemical properties. It also has provided an overview of strategies for preserving historical wood consolidation from a materials science perspective, summarizing, and analyzing the properties of traditional consolidation materials and their treatment methods over the past century. The review has highlighted the properties, consolidation mechanisms, and applications of novel bio-based nanocomposites and their latest research results in the context of sustainable development.

Traditional consolidation materials are mainly natural resins and organic materials, so it is difficult to use one material to solve all the problems of historical wood. Each substance has its own limitations and effects on wood. With the development of polymer materials and nanotechnology, consolidation materials are gradually changing from single natural resins to complex and diverse synthetic polymer systems, such as nanomaterials, organic/inorganic composite systems, biopolymer materials, and supramolecular polymer networks. The unique advantage of novel inorganic nanoparticles such as Ca(OH)$_2$, Mg(OH)$_2$ and CaCO$_3$ is that they can sustainably solve the problem of wood acidification. The organic/inorganic composite system consisting of Ca(OH)$_2$ nanoparticles with organosilicon compound and halloysite nanotubes improves the permeability of traditional single reinforcing materials such as silicone resins, beeswax, and polyethylene glycol in wood and gives them novel properties. Sustained deacidification while improving the mechanical strength of wood is sustainable and non-toxic, opening up a novel strengthening strategy for green and environmentally friendly wood artifacts, but still needs a lot of research to achieve wide application.

The most obvious advantage of natural biopolymers such as keratin, chitosan, cellulose, lignin and oligoamides over conventional materials is that biomass materials further enhance their compatibility with wood, under mild reaction conditions and from a wide variety of sources. Although these are still in the exploratory stage, they provide a solid foundation for research into fully reversible consolidation materials. Among them, the supramolecular polymer network constructed on the basis of chitosan and guar gum can simultaneously solve three major problems faced by historical wood: structural instability during drying, biodegradation, and chemical degradation caused by the acidic environment generated in water-saturated wood catalyzed by Fe$^{3+}$. This is difficult to achieve with traditional materials and is of epochal importance for the consolidation and conservation of wooden relics.

Overall, from traditional to new consolidation methods, with the application of new materials and technologies, the use of consolidation materials has shifted from the initial single objective of giving wood good dimensional stability to multiple objectives including retaining its integrity, biocompatibility, ecological sustainability, and treatment reversibility. Although no perfect consolidation material has been identified that meets all of these requirements, the progress that has been made from extensive experiments and studies that have been carried out in the early stages shows that the prospects for consolidation and conservation of historical wood are very promising and that sustainable methods of future conservation still need to be explored, primarily in the following aspects:

1. Further research into the modification of traditional consolidation materials (e.g., linseed oil with special heartwood extracts, tung oil mixed with beeswax to de-posit sodium chloride particles, etc.) can give new properties to the raw material, making the
original vegetable oil consolidation green and extending the service life of the wood. Conversely, improvements in the treatment of early consolidation materials are one way to decreased wood darkening after consolidation, for example by soaking it in a buffered solution before treating it with polyethylene glycol.

2. Bio-based materials are one of the primary research directions for future green consolidation materials due to their renewable nature, low cost, modification potential, and high compatibility with wood. Natural biopolymer materials such as proteins, cellulose, and lignin have hierarchical structures and functions that can effectively enhance wood tissue. With the advance of nanotechnology, nanoscale consolidation materials such as nanocellulose and lignin nanoparticles have also been derived, but further research is needed to improve and enhance color and permeability issues related to impregnation with nanoscale consolidation materials in order to exploit their potential to enter wood ultrastructure to the best effect.

3. On the basis of polymer chemistry and polymer material science, polymeric biopolymer materials such as chitosan with different degrees of polymerization and deacetylation and its tert-butylidimethylsilane derivatives (TBDMS-chitosan), synthetic cellulose derivatives, hydroxylated oligoamides, and organosilicon compounds can be synthesized to mimic the structural properties of natural compounds with high permeability, stability, and reversibility. These represent further providing more options for research into new reinforcing materials. Meanwhile, with the development of protection systems suited to the multiple needs of wood is an essential part of future research. For example, a supramolecular polymer network system (PolyCatNap) of catechol and naphthol-functionalized chitosan has been constructed to simultaneously address various problems faced in historical wood conservation, making it a safer and greener solution today.

4. Finally, the advantages of emerging technologies such as bionics and atom transfer radical polymerization in the design of polymer molecular structures and functions also provide opportunities and new ideas for the development of nanocomposites and bionic topologies more suitable for wood consolidation. However, these technologies are still in the laboratory exploration stage and need further in-depth research, especially to improve the dimensional stabilization effect, mechanical properties, environmental protection, and reversibility of wood treatments.

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