COMMENTARY

Preserving ancient artifacts for the next millennia

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When wood is kept dry, it can remain intact for millennia, as evidenced by numerous artifacts from ancient Egypt (1). However, when wood interacts with water, numerous problems arise that can cause the wood to become permanently damaged or destroyed completely. Wood exhibits swelling on moisture uptake and shrinkage on drying, and these cyclical moisture changes lead to internal stresses and can eventually form splits and checks within the wood. When there is an abundance of moisture in the wood, it is susceptible to microbial growth, fungal decay, corrosion of embedded metals, and chemical depolymerization from certain ions and free radicals. These moisture-induced damage mechanisms pose problems for conservation of wooden artifacts that were at one time waterlogged, notably recovered warships such as the Mary Rose. In PNAS, Walsh et al. (2) propose a way to protect historical artifacts from moisture-induced damage mechanisms by introducing chemicals that polymerize within the wood structure. The interpenetrating polymer network strengthens the artifact, while at the same time, functional groups on the polymers protect the wood from further breakdown by biodeterioration and chemically induced depolymerization.

Wood Damage Mechanisms

Wood is a cellular, orthotropic biomaterial; long, narrow cells are oriented along the root-to-crown direction of the tree. Depending on whether the wood came from a hardwood (angiosperm) or a softwood (gymnosperm), the size and structure of the cells will be different (3). However, regardless of the structural differences, chemically, wood cell walls are comprised of the same three structural polymers: cellulose, hemicelluloses, and lignin, in roughly the same proportions across species (4). The cell walls consist of highly oriented semicrystalline cellulose microfibrils in a matrix of amorphous cellulose, hemicelluloses, and lignin. Wood is hygroscopic and freely adsorbs or desorbs moisture from the environment until it reaches an equilibrium moisture content that depends primarily on the relative humidity. Moisture is believed to bind to sites in the amorphous regions of the cell wall (5). The adsorbed moisture causes swelling and internal stresses and facilitates diffusion of chemicals and ions through the cell wall.

Diffusion of ions and other chemicals through the cell wall structure is an essential part of wood damage mechanisms including biodeterioration (6), corrosion of embedded metals (7), and nonenzymatic depolymerization through the Fenton reaction (8). For example, corrosion of metals in wood involves the diffusion of chemicals from the wood to the metal surface where oxidation occurs. Corrosion products diffuse back into the wood where they can cause degradation of cellulose (9). Similar mechanisms have been identified as a key step in brown rot decay (10, 11). The fungus first secretes ferric ions, which then diffuse into the wood where they are reduced, eventually forming a hydroxyl radical that damages the cellulose. Diffusion of the Fe^{3+} ion into the wood and away from the fungal hypha is likely a necessary first step, as the hydroxyl radical would be harmful to the fungus. Clearly diffusion of chemicals and ions, especially ferric ions, is a necessary part of many wood damage mechanisms. Recently, it has been proposed that diffusion in wood cell walls occurs through interconnecting networks of moisture-softened hemicelluloses that are above their glass transition temperature (12), which occurs at room temperature or below when the moisture content is high (13). It follows that restricting the movement of the hemicelluloses or of the ferric ions themselves should prevent the above-mentioned damage mechanisms.

The polymer system presented by Walsh et al. gives insights into how damage mechanisms in wood may be stopped by restricting the movement of ions.

Recent Breakthroughs in Wood Protection

Walsh et al. present an entirely new way of protecting wooden artifacts through a four-part polymer system that forms a cross-linked network inside of the wood structure and binds to Fe^{3+} ions. The consolidant works in three ways (*i*): the polymer network provides mechanical support to the wood structure; (*ii*) antimicrobial-bacterial groups in the network protect against further biological attack; and (*iii*) the network binds to Fe^{3+} groups, rendering them immobile. Cleverly, the Fe^{3+} serves as a cross-linking site for the polymer network, meaning that the components can diffuse relative easily until they reach these sites. Furthermore, the areas with the highest concentration of Fe^{3+} are likely to be the areas with the most damage from biological or chemical processes and are in most need of the extra mechanical support from the interpenetrating polymer network. This synergistic action makes this a unique and promising consolidant for wooden artifacts. Walsh et al. also show that the polymer system can be used as an iron scavenger to remove high concentrations of ferric ions.

In a broader context, the polymer system presented by Walsh et al. gives insights into how damage mechanisms in wood may be stopped by restricting the movement of ions. Traditional wood protection treatments inject a biocide into the wood to stop biological attack by poisoning the organisms. Although Walsh et al. did not examine its effectiveness against wood decay fungi, the polymer network of Walsh et al. could conceivably be used to protect wood structures from decay by arresting the diffusion of iron ions away from the fungal hyphae. Such a use would have broad practical and scientific implications. Practically, its economic potential as

Author contributions: S.L.Z. wrote the paper.

The author declares no conflict of interest.

See companion article on page 17743.

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 www.pnas.org/cgi/doi/10.1073/pnas.1420835111

a structural wood protection system could be large; wood preservation is a USD 4 billion industry in the United States alone (14). Scientifically, the polymer network could be used to better understand the mechanisms of wood decay fungi. The exciting contribution by Walsh et al. could lead to breakthroughs that help both wooden artifacts and wood structures last forever.

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