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Processes and properties

Bio-inspired wood protection, modification and functionalization

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ABSTRACT

Wood is a versatile, natural, and environmentally friendly resource that has attracted attention as a material for sustainable building for many years. Recent advances in materials research have delivered several innovative solutions for the construction sector. However, intrinsic properties of wood affects its operational durability, which is still a limiting factor in many applications and environments. As a biological material, wood is sensitive to environmental conditions and microorganisms; therefore, wood products require additional protective measures to extend their service life in outdoor applications. Systems created by nature are valuable sources of inspiration for the development of new concepts, materials and solutions implemented in various fields, including structural engineering and the built environment. In recent years, possible benefits from concepts developed by nature have also become more interesting for sustainable materials design including wood protection and modification. This contribution provides an overview of inspiring phenomena occurring in nature that can be understood, transferred, and implemented to enhance various wood properties.

Keywords: Biomimicry, bioinspiration, wood protection, wood functionalization, wood modification

1. INTRODUCTION

Wood and engineered wood products serve as different types of loadbearing structures, as well as complementary constructive components, such as cladding, decking, doors, and windows. The performance and strength of wood used in structural applications are influenced by its physical properties, such as density, mechanical resistance, sorption and permeability, dimensional stability, thermal conductivity, acoustic and electric properties, natural durability, and chemical resistance. Other characteristics, such as appearance, smell, morphology, roughness, and surface texture influence material perception. Wood, as all biological-origin materials, possesses high natural variability, expressed in a wide range of intrinsic characteristics. This variation exists between species, trees, and even within a single trunk. Wood retains a wide range of colors, patterns or shine, depending on the species and manufacturing process.

The wood species differ in appearance but most of all in physical (hygroscopic properties, density, shrinkage-swelling, sound-, electro-, thermal- conductivity) and mechanical properties (strength, toughness, hardness, elasticity, plasticity, brittleness, wear resistance). Broad availability, relatively low maintenance cost, and simple processing leads to the frequent use of wood as a construction material for both interior and exterior applications. However, to make its applications even more broad, innovative and preferably environmentally friendly methods to overcome drawbacks of wood are highly desired.

Given the progress in science, and the development of modern and powerful analytical techniques, the structures and functions created by nature become an inspiration for discovery of new materials and alternative ways of production. During 3.8 billion years of evolution, organisms developed efficient and very often simple solutions, allowing full adaptation to the environment (Bhushan 2009). The results of those adaptations are available to scientists, who can observe and be inspired by nature's approach of using minimum materials for maximum effect. The largest area of biomimicry research is related to materials, accounting for around half the published research (Lurie-Luke 2014). Recent developments include smart materials reacting in response to external stimuli, novel materials capable of shape and structural arrangement, and a broad range of surface modifications. The success of bioinspiration depends on a good match between an engineering problem and a biological solution. This manuscript focuses on biological strategies that are or might be an inspiration for enhancing various wood properties.

2. IMPLEMENTATION OF BIOINSPIRATION FOR IMPROVEMENT OF PROPERTIES OF INTEREST

Examples of selected properties related to wood susceptibility to water and fire as well as two other aspects related to wood appearance: color and self-healing are briefly presented with an emphasis on the bioinspired concept used for their development.

2.1 Hydrophobicity

The hydrophilic character of wood can be reduced by surface and bulk treatments. The wettability of a surface depends on the surface chemistry, roughness, and surface energy of the solid, as well as the chemical composition and properties of the liquid. Water has a very high surface tension (72.8 mN \cdot m⁻¹); therefore, it tends to wet only surfaces bearing highly polar groups. Conversely, apolar liquids of lower surface tension produce drops that are flatter than those of water. The lowenergy surfaces (hydrophobic or oleophobic) are difficult to wet with water or apolar liquids. The wettability is usually determined by measuring the contact angle (CA) of a water droplet on a solid surface. In the case of a solid surface, when the CA of water is larger than 150°, it is called superhydrophobic (Guo et al. 2011). The accessible hydroxyl groups present in the chemical structure of wood components can be replaced by an esterification reaction resulting in bulking of the wood cell wall and improved dimensional stability of the entire material. The esterification of wood with various fatty acids provides a hydrophobic character to the material (stable CA values over time above 110°) with value oscillating around 140° for steaoryl chloride (C18) with concentrations of 0.1 M (Herrera Díaz et al. 2020). Moreover, the utilization of natural compounds like lignin for wood treatment can contribute toward reducing the hydrophilic character of wood (Gordobil et al. 2017).

The control of wettability is important from fundamental and practical perspectives, as superhydrophobic surfaces exhibit self-cleaning properties. The typical examples of superhydrophobic natural surfaces are lotus, rice, and taro leaf. They exhibit microscopic roughness on different length scales together with the presence of hydrophobic epicuticular wax crystalloids. The hierarchical structure of lotus leaf was the inspiration for the development of superhydrophobic surfaces by nanoscale casting (Si and Guo 2015) or UV-nanoimprint lithography (Lee and Kwon 2007). Other methods for obtaining superhydrophobic surfaces include wet chemical reaction, electrochemical deposition, self-assembly, layer-by-layer, and chemical vapor deposition (Guo *et al.* 2011). Superhydrophobic surfaces can be used to obtain anti-icing, super oil-repellent, anti-fogging, self-cleaning, or electrowetting effect, among others. Coatings offering the lotus effect dedicated to wood protection are already available on the market.

2.2 Fire resistance

Combustibility is a main limiting factor of wood which can be overcome by fire and flame retardants. The drawback of traditional treatments are the toxicity and volatility of some of their components and the loss of chemicals by leaching, leading to poorer fire performance and to reduced safety margins during use phase.

Natural compounds, such as tannin, treated lignin, and inorganic nanoparticles have been successfully implemented as biobased fireproof coatings for wood (de Hoyos-Martínez *et al.* 2021) in the frame of the NoMoreFire project. Another strategy, inspired by Canary pine bark architecture and chemistry, was proposed by Khalako *et al.* (2001). Researchers developed a type of macro-scaled multilayer structure similar to pine bark and developed a wood coating that delays ignition and fire propagation. An alternative way to improve the fire resistance of wood is through mineralization with calcium carbonate (CaCO₃). Several methods for this already exist, but their application requires expensive (supercritical CO₂) (Tsioptsias and Panayiotou 2011) or environmentally questionable (perfusion of wood with NH₃) steps (Hernandez *et al.* 2022). Biologically induced mineralisation (BIM), for the formation of amorphous crystals of CaCO₃, might be an interesting alternative to the above processes. A novel concept for mineralization of wood by means of selected fungi will be investigated in the newly funded project MICRO-INSERT.

2.3 Color

Tannins, pigments, and resins make wood colorful, ranging from whiteish in case of aspen to blackish in case of ebony. Several hardwood species (such as maple, oak, beech or elm) have the characteristic lustre that increases their glossiness. The anatomical structure of wood, including macro (yearly rings, hearth wood, knots) and micro features (fibres, weasels, rays) provide a unique texture that might be additionally emphasized by protective treatments, such as coating, impregnation, or oil/wax finishing.

Natural color of wood is often affected by wood decomposing fungi, which from the timber commodity perspective is considered as a defect and a source of lost economic value (Morris *et al.* 2021). However, what was for a long time considered as a shortcoming, might become a desired property. Wood spalting, a natural process, has recently garnered interest as a way of producing decorative wood products for niche markets. Moreover, fungal based pigments might be an interesting option for the development of environmentally friendly alternatives for textile coloration, optoelectronics, and wood protection (Van Court *et al.* 2021).

Structural color presents an interesting alternative to pigment-based methods for modifying appearance. Structural coloring is a visible consequence of a particular patterning of a reflecting surface with regular structures at submicron length scales (Dumanli and Savin 2016). This phenomenon is a result of diffraction, interference, or scattering of light and often appears as bright, shiny, metallic, or iridescent. Contrary to pigment colors, structural colors don't fade as they are not sensitive to chemical and environmental alterations. Understanding the material structure at the nano-level, together with development of new fabrication processes (patterning, etching, moulding, deposition), allows highly reproducible and high throughput microfabrication. The structural color can be generated by diffraction gratings (e.g., butterfly scales), thin-films

interference (e.g., insects wings), photonic crystals (e.g., marine animals, chameleons), and scattering (e.g., bird feathers). However, in nature, very often structural color is assured by merging different physical phenomena. Morpho butterfly wings combine multilayer interference, diffraction, scattering, and pigment-induced absorption to produce its singular, angle independent brilliant blue color (Dumanli and Savin 2016). Structural colors can be produced by the previously described strategies: top-down and bottom-up. Top-down includes various lithographic techniques that might use templates (photolithography, holographic lithography, nanoimprinting lithography, and soft lithography), or not (electron beam lithography, focused ion beam lithography, and scanning probe lithography), layer by layer deposition techniques (liquid or vapour based), interactive size reduction, or a combination of the above (Dumanli and Savin 2016). The bottomup strategies include self-assembly (colloidal, anisotropic particle, block copolymer) and biomimetic templates (direct or inverse). The method for development of photonic crystal coatings with structural color on the wood surface was recently presented by Liu et al. (2020). The photonic crystal structures were obtained by fabricating monodisperse microspheres of P(St-MMA-AA) using a facile sessile drop process. The structural colors of the photonic crystals were brilliant; monochromatic colors on wood were obtained by controlling the diameter of the assembled latex microspheres. Moreover, at different viewing angles variable color effects were observed, making the coating iridescent.

2.4 Self-repairing

Majority of the surfaces are exposed to conditions that cause damage, which reduces their functionality and requires reparation or replacement. The repairing mechanisms used in polymer composites can be achieved by two methods: molecular diffusion and thermally reversible solidstate reactions or by releasing healing agents stored in the material (Bhushan 2018). Speck and Speck (2019) divide self-repair mechanisms in higher animals and plants into an initial self-sealing phase and a subsequent self-healing phase. Self-sealing is limited to restoration of functionality, but the mechanical properties are not completely restored. The self-healing phase leads to structural reparation and restoration of mechanical properties. Self-sealing can occur within a few minutes (by filling wounds with latex, resin, mucilage), or hours (by overlapping wound sites, close contact of wound surfaces, rolling-in of wound edges). Self-healing is related to the formation of a ligno-suberized boundary layer and might take several days to weeks (Speck and Speck 2019). However, the self-repairing phenomena observed in biology is challenging for building materials. The project granted to Purdue University to develop a transformational "living" wood with the strength of steel, self-healing capability, and combined carbon-sequestering benefits from wood and microbes is currently under investigation. Development of wood protective coatings might be an alternative to bulk modification. A biofinish, where living Aureobasidium pullulans moulds regrow on a damaged wooden surface (Sailer et al. 2010, Poohphajai et al. 2021) is first proof of a concept solution. The synergy of bioinspired protection mechanisms, active biobased ingredients, and a living fungal biofilm are currently under investigation within the framework of the ARCHI-SKIN project. The project aims to comprehensively evaluate bioinspired strategies of the biofilms' chemical-structural-properties and develop a solid basis for the development of future Smart Living Surfaces. The coating formulation will be optimized for three types of substrates: bio-based porous, inorganic porous, and non-porous. It is expected that besides self-repairing (self-healing) by active damage repairing mechanisms, it will be bioactive (possess selective antimicrobial and antioxidant properties), fire-resistant, hydrophobic, UV-blocking, and will facilitate bioremediation by actively capturing toxic metals from the environment.

3. SUMMARY AND FUTURE CHALLENGES

The convergence of solutions developed by animals and plants indicate that nature has developed the most optimal solutions to solve specific problems. Such examples should be the first candidates for biomimetic implementation in engineering contests. As many other great ideas, biomimetics started from simple imitation of natural organisms. It has a great potential for finding new, innovative solutions for wood enhancement. The real challenge, however, is to achieve them with biobased ingredients, while providing environmentally friendly and sustainable solutions for wood protection.

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5. REFERENCES

Bhushan, B (2009): Biomimetics: lessons from nature – an overview. *Philosophical Transactions* of the Royal Society A, **367**, 1445-1486.

Bhushan, B (2018): Biomimetics Bioinspired Hierarchical-Structured Surfaces for Green Science and Technology. 3rd edition: Springer Nature Switzerland.

Dumanli, A G, Savin, T (2016): Recent Advances in the Biomimicry of Structural Colours. *Chemical Society Reviews*, **45**(24), 6698-6724.

Gordobil, O, Herrera, R, Llano-Ponte, R, Labidi, J (2017): Esterified organosolv lignin as hydrophobic agent for use on wood products. *Progress in Organic Coatings*, **103**, 143-151.

Guo, Z, Liu, W, Su, B L (2011): Superhydrophobic surfaces: From natural to biomimetic to functional. *Journal of Colloid and Interface Science*, **353**, 335-355.

Hernandez, V, Romero, R, Arias, S, Contreras, D (2022): A Novel Method for Calcium Carbonate Deposition in Wood That Increases Carbon Dioxide Concentration and Fire Resistance. *Coatings*, **12**, 72.

Herrera Díaz, R, Gordobil, O, de Hoyos-Martinez, P L, Sandak, A, Labidi, J (2020): Hydrophobization and Photo-Stabilization of Radiata Pinewood: The Effect of the Esterification on Thermal and Mechanical Properties. *Forests*, **11**, 1243.

de Hoyos-Martínez, P L, Issaoui, H, Herrera, R, Labidi, J, Charrier-El Bouhtoury F (2021): Wood Fireproofing Coatings Based on Biobased Phenolic Resins. *ACS Sustainable Chemistry & Engineering*, **9**(4), 1729-1740.

Khakalo, A, Jaiswal, A K, Kumar, V, Gestranius, M, Kangas, H, Tammelin T (2021): Production of High-Solid-Content Fire-Retardant Phosphorylated Cellulose Microfibrils. *ACS Sustainable Chemistry & Engineering*, **9**(36), 12365-12375.

Lee, S M, Kwon, T H (2007): Effects of intrinsic hydrophobicity on wettability of polymer replicas of a superhydrophobic lotus leaf. *Journal of Micromechanical Microengineering*, **17**(4), 687-692.

Liu, Y, Hu, J, Wu, Z (2020): Fabrication of Coatings with Structural Color on a Wood Surface. *Coatings*, **10**, 32.

Lurie-Luke, E (2014): Product and technology innovation: What can biomimicry inspire? *Biotechnology Advances*, **3**, 1494-1505.

Morris, H, Smith, KT, Robinson, SC, Göttelmann, M, Fink, S, Schwarze, FWMR (2021): The dark side of fungal competition and resource capture in wood: Zone line spalting from science to application. *Materials & Design*, **201**, 109480.

Poohphajai, F, Sandak, J, Sailer, M, Rautkari, L, Belt, T, Sandak, A (2021): Bioinspired Living Coating System in Service: Evaluation of the Wood Protected with Biofinish during One-Year Natural Weathering. *Coatings*, **11**, 701.

Sailer, M, van Nieuwenhuijzen, E J, Knol, W, (2010): Forming of a functional biofilm on wood surfaces. *Ecological Engineering* **36**,2, 163-167.

Si, Y, Guo, Z (2015): Superhydrophobic nanocoatings: from materials to fabrications and to applications. *Nanoscale*, **7**, 5922-5946.

Speck, T, Speck, O (2019): An Overview of Bioinspired and Biomimetic Self-Repairing Materials. *Biomimetics*, **4**, 26.

Tsioptsias, C, Panayiotou, C (2011): Thermal stability and hydrophobicity enhancement of wood through impregnation with aqueous solutions and supercritical carbon dioxide. *Journal of Materials Science*, **46**, 5406-5411.

Van Court R C, Vega Gutierrez P, Robinson S C (2020): Pigment Production by the Spalting Fungus *Scytalidium ganodermophthorum* and its Industry Potential. *Proceedings IRG Annual Meeting* IRG/WP 20-10957, 12pp.