## **Bio-Based Wood Protective Systems**

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Natural compounds and biopolymers materials contribute to protective matrices that safeguard wood surfaces against diverse challenges. Essential oils, vegetable oils, and bio-based polymers are explored for their potential in crafting ecofriendly and durable coating matrices.

Keywords: wood coatings ; bio-based additives ; green solutions ; wood protective systems

## 1. Introduction

Wood, a resource that has historically been extensively harnessed by humans <sup>[1]</sup>, owes its popularity to its unique physical and chemical attributes <sup>[2]</sup>. These characteristics encompass a remarkable strength-to-weight ratio <sup>[3]</sup> and ease of processing <sup>[4]</sup>. Moreover, wood's contemporary significance lies in its natural abundance, material simplicity, and distinctive aesthetic qualities <sup>[5]</sup>. However, the inherent lignocellulose composition of wood renders it susceptible to challenges such as flammability <sup>[6]</sup>, moisture-induced deterioration <sup>[Z]</sup>, and solar radiation-induced damage <sup>[8]</sup>. These processes impact wood's inherent durability, dimensional stability, and surface integrity, leading to notable structural and colour changes, along with a gradual reduction in resistance to biological agents and mechanical properties.

To address these concerns, organic coatings are commonly employed on wooden components, bolstering their resilience by providing defence against solar radiation <sup>[9]</sup>, humidity fluctuations <sup>[10]</sup>, chemical assaults <sup>[11]</sup>, mechanical stresses <sup>[12]</sup>, and the proliferation of harmful organisms, like fungi <sup>[13][14]</sup>, while preserving wood's aesthetic appearance.

The widespread application of wood in outdoor settings has motivated both academia and industry to explore innovative techniques for enhancing wood coatings  $^{[15]}$ . One such approach involves enhancing the ultraviolet (UV) absorption capabilities of wood coatings by incorporating various nanoparticles, such as TiO<sub>2</sub>  $^{[16]}$ , ZnO  $^{[17]}$ , SiO<sub>2</sub>  $^{[18]}$ , and CeO<sub>2</sub>  $^{[19]}$ . Similarly, nanostructures with enhanced hardness, stiffness, and thermal stability, like nanosilica  $^{[20]}$ , nanoalumina  $^{[21]}$ , nanoclay  $^{[22]}$ , and nanocellulose  $^{[23]}$ , have been utilized to augment the mechanical properties and water resistance of wood coatings  $^{[24]}$ . Additionally, the antibacterial and fungicidal properties of wood coatings have been fortified by the integration of nanomaterials, like copper nanopowders  $^{[25]}$ , nanotitanium  $^{[26]}$ , and silver  $^{[27]}$ .

Nonetheless, the emerging trend of using coloured paint to impart specific aesthetic effects to wooden products, employing novel pigments <sup>[28]</sup> and distinct gloss values <sup>[29]</sup>, is gaining traction in the wood protective coatings sector <sup>[30]</sup>. The stability of these pigments in wood paints has recently garnered significant attention <sup>[31]</sup>. It is crucial to ensure that the incorporation of innovative pigments delivers unique aesthetic effects without compromising the protective barrier properties of the organic coating. The combination of wood paints with different types of pigments may lead to significant challenges, such as reduced protective efficacy due to matrix discontinuities or concerns regarding the pigments' limited durability <sup>[32]</sup>.

## 2. Bio-Based Coating's Matrix

The matrix is the main constituent of a coating, with a fundamental function in the final protection provided by the coating layer. The research for the design of environmentally friendly and eco-sustainable coatings starts, therefore, from the identification of natural compounds to be employed as matrix constituents. Essential oils occupy a large fraction of the research in this field. Essential oils can be directly used for wood impregnation, or they can either be supplemented with particles or employed as starting material for the synthesis of organic coatings. Alternatively, the matrix of wood coatings might be synthetized starting from bio-based polymers, of which chitosan, cellulose, and lignin are the most famous.

#### 2.1. Vegetable Oils and Their Derivatives

Vegetable oils represent a "green" and eco-friendly solution to be used as wood coatings and preservatives. In fact, many essential oils, and some of their derivatives, have been known since ancient times for their antimicrobial or antifungal effects <sup>[33]</sup>. Another advantage of vegetable oils is the fact that they induce a smooth feel and provide the coated surface with a small coefficient of friction <sup>[34]</sup>. Natural oils can be directly applied to the wood surface, but they may also serve as the starting point for the synthesis of the bio-based coating matrix.

Oils can be classified as drying and non-drying. The former become harder when exposed to the atmospheric environment. On the other hand, non-drying oils remain in the liquid state and are, in general, not useful for the production of coatings. Indeed, coatings should be able to provide protection to the wood substrate, remaining adhered and intact, even when the wood object is moved, touched, or simply exposed to aggressive environmental conditions. The hardening process occurs because drying oils possess functional groups that are able to react and be oxidized by atmospheric oxygen <sup>[35]</sup>. Linseed oil and tung oil represent the most known and explored drying oils in the field of coatings. Linseed oil, alternatively referred to as flaxseed oil or flax oil when used for consumption, is a clear to slightly yellow oil derived from the matured, dried seeds of the flax plant (scientifically known as *Linum usitatissimum*). The oil can be acquired through a process involving pressing and, occasionally, solvent extraction. Similarly, tung oil, also known as China wood oil, is a drying oil derived from pressing the seed found within the nut of the tung tree, scientifically known as *Vernicia fordii*. When exposed to air, tung oil undergoes a process of polymerization, causing it to harden. This results in a transparent finish with a rich, almost glossy appearance, akin to a wet surface. It is primarily employed for the purpose of enhancing and safeguarding wood. Both tung and linseed oils provide hydrophobicity to the wood's surface, but some differences in their performances have been reported <sup>[36]</sup>. On one hand, tung oil provides a hydrophobic effect that can be appreciated soon after its application; on the other hand, linseed oil requires a longer time to complete film formation.

In addition to the protective effect provided by the oil, additives and/or pigments can be added to increase the performance of the coating. The presence of pigments and additives will certainly have an influence on the degree of wear and decay upon weathering <sup>[37]</sup>. For example, the addition of 5% hemp-derived biocarbon (BC) to tung oil resulted in increased hydrophobicity of the coated surface. Although the degree of hydrophobicity did not directly correlate with the amount of introduced BC, a higher BC content was associated with improved protection against the weathering effects <sup>[38]</sup>. Pigments extracted from wood-decay fungi solubilized in raw linseed oil could extend the service life of the coating <sup>[39]</sup>, while the addition of nanofibrillated cellulose (NFC) has been reported to improve the wear resistance of linseed oil-based coatings <sup>[40]</sup>.

In addition to directly treating the wood surfaces with oil as it is, another solution is to use oils of natural origin as a starting base for the synthesis of resins and coatings. For example, a bio-based epoxide amine nanocoating was synthesized starting from tung oil. The novel resin coating was found to enhance the density of the wood material, decrease water absorption, and improve the mechanical properties of the wood's surface [41]. Acrylated vegetable oils have been used for the production of wood coatings, either in combination with propoxylated glycerol triacrylate <sup>[42]</sup> or together with a photoinitiator for the induction of the curing process [43]. A few years ago, Wang et al. exploited castor oil as a starting material to synthesize a multifunctional castor oil-based bio-mercaptan, with the addition of an organic phosphorus flameretardant [44][45]. This wood coating promoted the degradation of films at lower temperatures, but, at the same time, it could reduce the maximum degradation rate and could delay the process of decomposition as well. In a different study, a transparent castor oil-based coating was successfully produced by combining siloxane oligomer and castor oil through epoxidation [46]. The coating object of the study contained grafted polydimethylsiloxane molecules that were associated with the provided roughness and surface morphology, and responsible for a reduced friction coefficient with oily contaminants. In a different study, epoxidized soybean oil was mixed with castor oil maleic anhydride adduct (COMA), which is "green" and environmentally sustainable because it is obtained from renewable materials, and methyl nadic anhydride (MNA), with the aim of generating a wood coating with a high content of renewable materials [15]. Castor oil is much exploited in the context of bio-based coatings, since it offers varying applications and the possibility to be modified to improve its properties, both in terms of protection and in terms of durability.

Another natural oil with a putative potential for wood protection is extracted from the seeds of the soybean. Among the many studies available in the literature, Li et al. reported that soybean oil could improve the functional performance of a waterborne polyurethane acrylate resin. After modification with acrylic acid, the researchers introduced the modified epoxy soybean oil into the resin, and this resulted in a fast-curing resin that provided good mechanical and thermal properties to the wood substrate <sup>[47]</sup>.

Despite being less exploited compared with other most famous essential oils, peanut oil also represents a source of bioprecursors for the design of wood coatings. In the study published by Raychura and co-workers, N,N-bis(2-hydroxyethyl) fatty amide was produced from peanut oil and used as precursors for the synthesis of polyurethane <sup>[48]</sup>. The obtained wood coating displayed excellent behaviour, both in terms of mechanical and thermal properties, but also antimicrobial and chemical resistance, representing a valid alternative in substitution of petroleum-based coatings.

In addition to the most explored vegetable oils, for which many studies can be traced in the literature, other less-known oils of natural origin have been investigated for their potential to provide a barrier effect to wood. The Mahua tree is a medium/large-sized tree, which mostly grows in India. The oil extracted from this plant was identified as a possible precursor for the synthesis of polyurethane. Mahua oil was indeed used as raw material for the synthesis of polyetherimide polyol, and the consequently obtained polyurethane displayed high resistance to water, solvents and chemicals, and good mechanical, thermal, and antimicrobial properties <sup>[49]</sup>. Once again, the oil extracted from the seeds of *Jatropha curcas*, a plant typical of tropical regions, was combined with vegetable resins, and the performance of the obtained coating was assessed based on the physical properties of Ayous wood. Despite the reference varnish being more protective against fungi, the newly produced bio-based coating had a higher protection against termite attack <sup>[50]</sup>, suggesting the possible wood-protection potential of extracts from these plants.

#### 2.2. Natural Biopolymers for Wood Protection

Natural biopolymers, including the most famous chitosan and cellulose, are promising solutions to be used for wood protection. The drying behaviour of three natural biopolymers was investigated in the context of the preservation of archaeological wooden objects, namely chitosan, alginate, and cellulose <sup>[51]</sup>. The study concluded that chitosan and alginate improved the thermal stability of wood and could thus be considered as potential wood consolidants. However, cellulose nanocrystals did not display good performance in terms of wood protection, being, therefore, less promising in this field of application <sup>[51]</sup>.

Chitosan is a natural biopolymer that can be isolated from the outer shells of shrimps and crustaceans. The potential of chitosan for the development of bio-based wood coatings has been widely explored. Woźniak et al. used chitosan to limit the leaching of caffeine out from the wood substrate. Indeed, despite having anti-fungal activity, caffeine is extremely prone to leaching in the presence of water, considerably limiting its exploitability, especially considering that outdoor wood objects are frequently exposed to conditions of potentially high humidity. While the wood treated just with caffeine had reduced anti-fungal activity and a mass loss of about 21%, the chitosan–caffeine preparation extended the resistance of wood owing to the limited caffeine leaching provided by the chitosan [52]

One of the main damaging factors for coated wood surfaces is exposure to UV radiation. Janesch and colleagues attempted to deal with this issue by creating layer-by-layer coatings with chitosan and  $CeO_2$  nanoparticles as UV-protective molecules <sup>[19]</sup>. Owing to the addition of the  $CeO_2$  nanoparticles, the colour variation induced by exposure to UV rays was considerably reduced, especially the yellowing of the wood surface, which is a characteristic outcome when the wood substrate is exposed to solar radiation.

Cellulose nanofibril (CNF) is one of the most abundant and common biopolymer nanofibrils, and it possesses good qualities for it to be employed as a bio-carrier for coating formulation. Yuan et al. combined CNF with graphitic carbon nitride nanosheets (gCNNS) as a UV absorber to shield the wood material from UV radiation <sup>[53]</sup>. After 15 days of accelerated weathering, the gCNNS/CNF coating significantly improved the colour stability of the wood substrate, suggesting the excellent performance of this complex formulation as a barrier to UV radiation.

As one of the most common biopolymers, several studies have explored the characteristics of lignin for the development of wood coatings. For example, lignin-based polyurethane coatings have been produced, with a high content of lignin. When compared with the uncrosslinked lignin precursor, the new polyurethane coating had higher thermal stability and hydrophobicity, suggesting that this may represent a new direction to generate novel bio-based coatings <sup>[54]</sup>.

## 3. Bio-Based Preservatives and Impregnators

One of the most immediate barriers to counter the weathering and/or biological-induced decay of wood is the application of preservatives or impregnators on wood samples. The manifested trend toward environmental sustainability and eco-friendly solutions calls for the need to shift from the classical chemical wood preservatives, which can be harmful to the environment, toward bio-based products. A comparative study was conducted to investigate the impacts and effectiveness of bio-based and commercially available chemicals for wood preservation <sup>[55]</sup>. According to the documented results, Colatan GT10, a Quebracho tannin mix, was identified as the most promising bio-based wood preservative, with lower

toxicity compared with copper-based chemicals, which are frequently commercially sold. Although it is generally assumed that bio-based chemicals have lower ecotoxicity, this is not always true. As pointed out in the same study, in some circumstances, bio-products may be even more toxic than the commercially available ones, highlighting the importance of conducting extensive ecotoxicity studies before the employment of a product and carefully investigating the environmental effects possibly associated with it <sup>[55]</sup>.

Several natural wood preservatives are extracts derived from plants and from vegetables. They include plant essential oils as well as plant extracts, containing several and varying active molecules. For example, stilbenes have been investigated as possible impregnators for Scots pine sapwood (*Pinus sylvestris* L.). The impregnation of wood with crude heartwood extract containing the stilbenes pinosylvin (PS) and pinosylvin monomethyl ether (PSM) was able to reduce fungal growth and, consequently, the decay of the material <sup>[56]</sup>. The main issue related to stilbenes is that they are prone to fungi-induced degradation, especially by *Rhodonia placenta*. Positive outcomes were obtained from pyrolysis distillates from the bark of spruce, which could inhibit fungal growth over 40% at a concentration of 0.1% <sup>[57]</sup>.

Tannins, of which many plants are a great source, are among the most explored and investigated natural extracts with potential as antifungal agents. Low concentrations of tannins extracted from cones of spruce and pine and from spruce barks could inhibit the growth of brown-rot fungi. However, they could not block the growth of white-rot and soft-rot fungi <sup>[58]</sup>. Therefore, although tannins might constitute promising agents for wood preservation, further deeper investigation is required. In a later study <sup>[59]</sup>, tannins were reported as natural wood preservatives, where they could improve resistance toward the white-rot fungus *Pycnoporus sanguineus* at a comparable level to that of the chromate copper borate preservative. The potential inhibitory characteristics of valonia, chestnut, tara, and sulphited oak tannins were also tested.

Caffeine is an alkaloid that can be easily extracted from plants. This widespread natural compound has been found to improve the resistance of spruce wood against termites and brown-rot fungi. The main drawback is that caffeine is prone to leaching out from wood in the presence of water, making it not perfectly suitable for the treatment of outdoor wood <sup>[60]</sup>.

Since ancient times, essential oils have been widely applied for different purposes. Considering their long history of use, also in the traditions of ancient local civilizations, they represent a valid and promising alternative as wood preservatives. In fact, many essential oils are reported to have anti-fungal properties. For example, essential oils extracted from *Lippia origanoides* displayed elevated anti-fungal properties, and the effect was attributed to the presence of thymol <sup>[61]</sup>.

Finally, one of the most environmentally sustainable lines of research involves the recovery of active substances from waste products. This offers the dual advantages of having a recyclable raw material, instead of searching for new sources, and reusing a waste product, thus reducing the issues related to waste disposal. Coffee silverskin is the perfect example of an extremely diffused industrial waste derived from the process of coffee roasting. Its potential for wood preservation was first explored by Barbero-Lopez et al. However, the results were not encouraging, as the authors showed that coffee silverskin was not as effective as commercial wood preservatives, despite being able to inhibit fungal growth at a level of 60–70% <sup>[62]</sup>. Nevertheless, it is highly likely that, in the future, research will be aimed at more deeply investigating industrial waste products as possible sources of active agents for their ultimate application as wood preservatives.

## 4. Bio-Based Fillers

The renewed attraction towards wood as a building material is driven by growing concerns about sustainability and evolving aesthetic preferences. Nevertheless, due to its organic nature, wood is vulnerable to changes in humidity and exposure to UV radiation. These factors instigate the creation of unstable molecules and lead to the breakdown of its lignin and cellulose constituents <sup>[9]</sup>. When used outdoors, wooden structures can experience issues like expansion, susceptibility to mould and fungi, changes in colour, yellowing, and a decline in both gloss and structural integrity <sup>[63][64]</sup>. As a result, the industrial field is progressively focusing on utilizing novel bio-derived additives in wood coatings. These fillers have the potential to enhance the component's ability to withstand weathering, serve as strengthening agents, or afford properties, such as antibacterial, antifungal, or flame retardant capabilities, as summarized in **Figure 1**.

# **BIO-BASED FILLERS**



Figure 1. Illustration of the functionality of bio-based fillers in wood protective systems.

#### 4.1. Weathering Resistance Bio-Based Fillers

Certainly, ensuring the ability to withstand weathering is a crucial factor for a wood coating, given that wood is especially vulnerable to the effects of outdoor elements. Bearing this in mind, different varieties of bio-derived additives have recently exhibited impressive performance in enhancing the coating's longevity. As a result, they contribute to prolonging the lifespan of outdoor wood components.

For instance, hemp-based biocarbon (BC) particles have been incorporated into tung oil to function as UV absorbers <sup>[38]</sup>. The introduction of these particles led to an enhancement in the water-repellent characteristics of the coating and resulted in improved colour preservation throughout the on-site weathering examination. Likewise, Nowrouzi et al. <sup>[65]</sup> utilized olive leaf extract as a supplement in polyacrylate coatings along with  $TiO_2$  or ZnO nanoparticles and a UV-absorber of the 2-(2-hydroxyphenel)-benzotriazole (BTZ) type. This combination was investigated for its ability to withstand natural or accelerated weathering. The study emphasized a decrease in the occurrence of wood discolouration due to the inclusion of olive leaf extract, which enhanced resistance against UV radiation.

Lignin itself stands as another interesting functional asset. Indeed, Zikeli et al. <sup>[66]</sup> extracted lignin from wood waste, utilizing a non-solvent technique to produce lignin nanoparticles (LNPs). Consequently, wooden specimens that were dipcoated with these LNPs exhibited encouraging surface alterations reminiscent of a cohesive film composed of merged LNPs. These treated samples demonstrated notably superior performance in simulated weathering trials compared with untreated control samples. Much like lignin, tannins, which are also derived from wood, offer an opportunity to enhance the protective qualities of coatings.

Lastly, carnauba wax has been combined harmoniously with zinc oxide nanoparticles within multi-layer coatings to thwart the deterioration and extend the lifespan of timber <sup>[67]</sup>. The resultant coating exhibited a distinct blend of superhydrophobicity, exceptional moisture buffering capacity, and partial UV shielding. This achievement was realized through an eco-friendly coating procedure, contributing to the preservation of wood's innate look and enhancing indoor air quality and comfort.

#### 4.2. Reinforcing Bio-Based Fillers

Similar to the necessity for weather endurance, wood coatings must also exhibit favourable mechanical attributes, encompassing traits such as hardness and resistance to abrasion. Once again, an array of bio-derived additives can be harnessed to enhance the capabilities of protective layers, infusing multifaceted functionality into the polymer matrix of the coating.

For instance, a recent study aimed to unveil the combined effects of two natural additives on the longevity and protective attributes of a bio-based wood coating <sup>[68]</sup>. This research highlighted the intriguing synergy between spirulina and wax, which afforded vivid colouring and specific aesthetic qualities to the paint. Additionally, they enhanced the surface's water-repellent characteristics and increased the abrasion resistance of the composite layer.

Likewise, consistent with strategies aimed at reinforcing the coating's ability to withstand environmental influences, the primary focus lies on utilizing lignocellulose material to elevate the mechanical attributes of the coating.

Nevertheless, cellulose currently stands as the material with the most significant capacity for enhancing the protective qualities of wood coatings. Indeed, both the industrial sector and academia are profoundly focused on exploring the protective attributes offered by cellulose derivatives. On a broader scale, an investigation aimed at unveiling the impact of a substantial concentration of cellulose fibres on the durability and protective characteristics of a bio-based wood coating <sup>[69]</sup>. The study focused on the advantages and disadvantages associated with the extensive incorporation of cellulose fibres as fillers in wood paint. It cautioned against an overabundance of these fibres, indicating the necessity for a defined threshold to prevent significant alterations in the coating's composition and subsequent weakening of its protective attributes. However, the optimal capabilities of cellulose can be harnessed most effectively on a nanoscale level.

#### 4.3. Bio-Based Additives for Antimicrobial Wood Systems

Over time, wood preservatives have seen a steady enhancement in their effectiveness, safety during usage, and ecofriendliness. This progress has been driven by the gradual replacement of certain chemical elements, prompted by concerns about their efficiency and impact on the environment. While numerous wood preservatives effectively hinder fungal decay, their adverse environmental effects have led to restrictions on their usage in numerous countries.

Hence, there is a notable ongoing pursuit for novel, ecologically friendly, and environmentally conscious antimicrobial supplements. In particular, researchers are exploring inventive bio-based fillers to enhance wood coatings, equipping them with the ability to combat fungi. This is vital because fungi pose a significant risk to the durability of wooden materials.

Considering this, a recent investigation conducted an assessment of the impact of certain chosen organic substances and modified versions thereof (including tea tree oil, propyl gallate, hydrogenated gum oil, salicylic acid, cinnamon bark oil, butylene oxide, and furfural) on the suppression of blue stain and mould fungi <sup>[70]</sup>. The study's findings indicated that salicylic acid, tea tree oil, and cinnamon bark oil exhibited the lowest level of mould proliferation following a four-week exposure within a mould chamber experiment. However, the literature is full of recent studies on the fungicidal effect of natural extracts.

Natural oils represent another category with efficient fungicidal performance, specifically analysed in recent years. For example, Moutaouafiq et al. <sup>[71]</sup> examined the antifungal effects of essential oil from *Pelargonium graveolens* and its constituent fractions on four wood-decaying fungi (*C. puteana, Coriolus versicolor, Poria placenta*, and *G. trabeum*). Their aim was to showcase the value of Moroccan aromatic and medicinal plants. The study revealed impressive outcomes, implying the potential utilization of this substance for safeguarding wood against fungal deterioration. Likewise, a recent study concentrated on creating an environmentally conscious wood preservative solution using distillate derived from the pyrolysis of coconut shells (CSPOD) <sup>[72]</sup>. The notable presence of phenolic compounds within the oil distillate conferred considerable resistance to decay in the treated wood, effectively combatting both white-rot and brown-rot fungi. Consequently, the potential exists for CSPOD to be refined into a formulation for wood preservation.

In addition to being a positive reinforcing filler, cellulose has been shown to act as a bio-based fungicidal additive. Jusic et al. <sup>[73]</sup> enhanced a standard commercial acrylic varnish by incorporating CNC and lignin sourced from beech wood. However, the resulting protection against bacterial deterioration was found to be inadequate. On the other hand, in another work, CNC led to an enhancement in fungal resistance <sup>[74]</sup>. This improvement was evident through decreased mass loss and changes observed in FTIR spectroscopy, attributed to the formation of crosslinks. These crosslinks also contributed to a reduction in water absorption.

Additional extracts from wood, such as tannins, can exhibit remarkable antimicrobial capabilities. Anttila et al. <sup>[58]</sup> directed their attention towards utilizing condensed tannins sourced from conifer trees as eco-friendly alternatives to synthetic wood preservatives. They extracted eight distinct tannin fractions from spruce cones, spruce barks, and pine cones. The research findings highlighted that, even at minimal concentrations, these tannins effectively restrained the growth of brown-rot fungi. On the other hand, Tomak et al. <sup>[75]</sup> infused Scots pine wood specimens with varying concentrations of valonia, chestnut, tare, and sulphited oak tannins at levels of 3%, 5%, 10%, and 15%. These treated samples were

subsequently exposed to attacks by the brown-rot fungi *C. puteana* and *Postia placenta*, as well as the white-rot fungi *T. versicolor* and *Pleurotus ostreatus*. The aim was to identify the most suitable tannin type and optimal concentration required to ensure effective resistance against decay. Tannins demonstrated their efficacy in suppressing brown-rot fungal assaults when no leaching was performed prior to the decay assessment.

#### 4.4. Green Flame Retardant and Intumescent Systems

Since the 1970s, flame retardants have been utilized in a wide array of consumer and industrial goods with the aim of diminishing a material's susceptibility to ignition or serving as a barrier (absorbing heat) to combustion. Notably, substantial emphasis has been placed on synthetic fire retardants throughout this time period. A considerable portion of commercially accessible flame retardants comprises organic compounds derived from oil sources (such as organo-halogenated, organo-phosphorous, and organo-nitrogen compounds). However, owing to their reliance on petroleum, these compounds face concurrent challenges, including depleting petroleum resources, geopolitical complexities, and contributions to global warming.

Given this perspective, recent developments have highlighted the effectiveness of vanillin as a promising bio-based option. For instance, Li et al. <sup>[76]</sup> successfully synthesized an innovative epoxy reactive flame retardant with phosphate content. This was achieved through a single-step reaction involving vanillin and benzene phosphorous oxydichloride (BPOD). Comprehensive analyses demonstrated marked enhancements in both the thermal stability and flame retardancy of the environmentally friendly coatings. As a result, this study introduced a sustainable and eco-friendly approach to crafting flame-retardant wood coatings, showcasing substantial potential for applications in the realm of wood-related endeavours. Similarly, Huang et al. <sup>[77]</sup> synthesized a polybasic carboxylic acid (HCPVC) by combining vanillin and hexachlorocyclotriphosphazene. This compound was utilized as a curing agent in a wood epoxy coating. Consequently, the resultant coating displayed an elevated char yield alongside notable flame retardant properties.

In a recent development, Trovagunta et al. <sup>[78]</sup> conducted an assessment of the viability of suberin, a bio-polyester found in cork, for the creation of bio-based flame-retardant substances. Meanwhile, Li et al. <sup>[79]</sup> accomplished the synthesis of a bio-based co-curing agent that imparted flame-retardant capabilities to both epoxy and wood. This innovation was aimed at constructing functional thermosetting coatings with enhanced flame resistance.

Continuing the exploration of environmentally friendly additives, Song et al. <sup>[80]</sup> successfully produced a bio-derived flameretardant curing agent for ammonium hydrogen phytate (AHP). This was achieved through the precise control of the molar ratio between phytic acid and urea in the reaction process. When compared with a control sample of wood coating prepared with a commercial curing agent containing ammonium chloride, the resulting wood coating (referred to as MP) not only showcased significantly enhanced thermal stability and flame retardancy, but also demonstrated comparable characteristics in terms of Tg, hardness, adhesion, and water resistance. Notably, the preparation process for MP was straightforward, amenable to scaling up, and employed an environmentally friendly water-based solvent. This study presents a sustainable and ecologically mindful approach to developing high-performance, flame-retardant wood coatings, showing substantial promise within the wood and furniture industries.

## 5. Bio-Based Pigments and Dyes

#### 5.1. Natural Pigments

Contemporary society is realizing that industrial waste frequently holds untapped potential that can be valued and utilized for other purposes. This principle applies to various industries, including wood coatings, where there is a growing inclination to seek novel pigments and additives. These components not only impart distinct colours to coatings, but also align with environmental considerations and the principles of a circular economy.

Considering this perspective, a recent investigation explored the pros and cons of utilizing pigment from spirulina as a natural colourant for wood treatment solutions <sup>[81]</sup>. Spirulina (*Spirulina platensis*) is a type of cyanobacteria acknowledged as one of the most prominent microalgal reservoirs for the industrial synthesis of phycobiliproteins <sup>[82][83]</sup>, encompassing light-harvesting protein pigments. The study highlighted the impressive colour effects achieved with the introduction of a spirulina-based additive. Nevertheless, the natural pigment showed notable issues related to its susceptibility to UV-B rays, which could lead to the degradation, as well as the potential fading, of the phycocyanin part present in spirulina. As a result, research underscores the significance of adopting suitable precautions to protect bio-based pigment from external elements, like temperature, sunlight, and liquids. Therefore, from this standpoint, a subsequent study aimed to uncover the combined effects of two natural additives on the endurance and protective characteristics of a bio-based wood paint <sup>[68]</sup>. While spirulina is utilized as an organic pigment, carnauba wax serves as a versatile filler. The analyses demonstrated

the impressive colouring capability of spirulina, imparting a distinct green hue to the paint and enhancing its reflective properties.

However, a recent investigation has also assessed the coloration impact of an eco-friendly black pigment sourced from discarded wood materials and incorporated into a bio-based wood paint <sup>[84]</sup>. The pigment was created by utilizing wood waste originating from industries such as paper, lumber, furniture, and flooring. To produce the pigment, the wood underwent a heat treatment within oxygen-free chambers. This controlled environment prevented the wood from combusting and releasing  $CO_2$  into the atmosphere. Consequently, the wood underwent a process of carbonization, effectively capturing the carbon that would typically be emitted during wood combustion. This unique characteristic led to the pigment being categorized as carbon-negative. The thermal energy and biogas generated during the manufacturing process were harnessed to power certain sections of the facility and produce the exclusive pigment itself.

#### 5.2. Microbial Pigments

Since ancient eras, organic dyes have served as colour enhancers in wood applications. Their environmentally friendly and health-conscious attributes, stemming from qualities like safety, non-toxicity, absence of carcinogenicity, and biodegradability, have aligned well with the growing emphasis on ecological considerations and human well-being. Consequently, microbial pigments present a promising avenue for industrial implementation, given their abundant availability, diverse range, rapid reproduction rates, and the flexibility of their cultivation without temporal or spatial constraints.

With this perspective in consideration, a recent study conducted by Liu et al. <sup>[85]</sup> assessed the potential advantages and obstacles associated with the utilization of microbial dyeing techniques for pigment incorporation in wood processing. Scholars have extensively presented and examined two viable approaches for integrating microbial pigments into the wood dyeing sector. One method involves inoculation, a straightforward and efficient technique where microorganisms deposit pigments onto or within the wood. However, this approach necessitates the industrial foundation of microbial screening and induction, along with the required equipment for ensuring industrial scalability. The alternative approach entails employing extracted pigments secreted by microorganisms for wood dyeing. This method offers relatively easier industrialization prospects. However, it entails technical challenges such as achieving mass production, establishing clean pigment-extraction methods using resoluble solvents, and addressing the deep penetration and stability of pigments within the wood.

## 6. Conclusions

In conclusion, the comprehensive exploration of natural compounds, biopolymers, and innovative materials for wood coatings underscores the industry's commitment to environmentally friendly and sustainable solutions.

Despite notable progress, the world of wood coatings grapples with persistent complexities. These include ensuring coating stability, addressing leaching risks, and targeting harmful microorganisms, biofilms, and wood-damaging pests while protecting non-target species. While aiming for high-performance coatings through intensive research, it is crucial to consider consumer preferences for economically feasible solutions. The introduction of nanotechnology raises valid health concerns about potential nanoparticle release from coatings on wood surfaces. To tackle these challenges, a comprehensive interdisciplinary approach is not just beneficial, but essential in enhancing wood durability. Coatings need to embody stability, efficiency, environmental responsibility, biological compatibility, inherent biodegradability, and practical cost-effectiveness. Through these integrated efforts, the evolution of wood coatings can align with sustainability and innovation principles.

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