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# Recent Developments and Trends in Sustainable and Functional Wood Coatings

Véronic Landry<sup>1,2</sup> · Gabrielle Boivin<sup>3</sup> · Diane Schorr<sup>3</sup> · Marie Mottoul<sup>1,4</sup> · Alex Mary<sup>2</sup> · Liza Abid<sup>5</sup> · Maylis Carrère<sup>2</sup> · Bertrand Laratte<sup>6</sup>

#### Abstract

**Purpose of Review** In the last decade, a transformation has occurred in the coating industry. While, in the past, the industry was primarily focused on reducing volatile organic compounds (VOC) and formaldehyde emissions, it is now circularity driving this industry. In this paper, we present several advances that have been made, as well as key trends in the wood coatings industry.

**Recent Findings** Replacing petroleum-based chemicals in coating formulations is at the heart of current research. In recent years, various biosourced molecules from animal and plant sources have been the subject of many studies aiming to incorporate them in coatings. Despite all the progress made in the last few years, coating producers are still facing many challenges regarding the availability and quality of biobased raw materials and balancing performance versus cost.

**Summary** While most of the sustainable coating solutions discussed in this review focus on well-known and widely accepted coating chemistries and technologies (water-based and photopolymerizable polyurethanes (PUs), acrylics, and epoxies), we also present new technologies that are expected to gain significant importance in the next few years such as layer-by-layer (LBL), polyelectrolyte complexes, and isocyanate-free PU.

Keywords Sustainable coatings · Circular economy · Biobased · Stimuli-sensitive coatings · Additives

Marie Mottoul and Alex Mary contributed equally to this work.

Véronic Landry veronic.landry@sbf.ulaval.ca

- <sup>1</sup> Department of Wood and Forest Sciences, NSERC–Canlak Industrial Research Chair in interior Wood-Products finishes, Université Laval, Québec, QC G1V 0A6, Canada
- <sup>2</sup> Department of Wood and Forest Sciences, NSERC
   Industrial Chair on Eco-Responsible Wood Construction (CIRCERB), Université Laval, QC G1V 0A6 Québec, Canada
- <sup>3</sup> FPInnovations, 1055 Rue du Peps, Québec, QC G1V 4C7, Canada
- <sup>4</sup> Chemistry Department, Faculty of Science and Engineering, Université Laval, 1045 Avenue de La Médecine, Québec, QC G1V 0A6, Canada
- <sup>5</sup> Department of Wood and Forest Sciences, Université Laval, Québec, QC G1V 0A6, Canada
- <sup>6</sup> Arts Et Métiers Institute of Technology, Campus de Bordeaux, Esplanade Des Arts Et Métiers, 33405 Talence, France

#### Introduction

Several initiatives have been implemented in recent years to increase the use of wood in buildings and interiors. Such strategies are fostered by the fact that wood is the only renewable construction material and is associated with the lowest  $CO_2$  emissions. Moreover, wood is linked to occupant comfort and well-being when used in building interiors [1] and is a material whose aesthetics are recognized and appreciated. Despite these undeniable advantages, using wood as a material still presents challenges in terms of its durability. It is sensitive to mechanical aggressions and prone to biological attacks and photodegradation. It must therefore be adequately protected so its appearance and properties last over time.

Coatings have long been used to protect, modify, or preserve the appearance and properties of wood. In recent years, the coating industry has been experiencing growing pressure to reduce volatile organic compounds (VOC) and formaldehyde emissions and their overall environmental impact. While sustainability in the coatings industry has long been synonymous with tightening VOC regulations, the industry now focuses more on circularity (circular economy) (Fig. 1). Greater emphasis has therefore been placed on responsible sourcing, i.e., using biobased, safe, and non-toxic compounds, reusing, and repurposing. A growing number of resin manufacturers are now turning to sustainable chemistry and are using the 12 principles of green chemistry to guide their product development [2]. Considering that approximately 40% of greenhouse gas (GHG) emissions come from the materials themselves, this transition towards greener chemistry is expected to intensify over the next few years.

This review outlines the principal regulations that apply to the wood coatings industry and the latest developments in the use of alternative raw materials to replace petroleumbased compounds. Functional and smart coatings that have the potential to lessen the environmental impact of coatings or to promote the use of wood as a green material are also presented in this review.

#### The Transformation of the Coatings Industry

The coating industry has transformed rapidly in recent years. One of the reasons for this is the urgent need to reduce GHG and VOC emissions, which affect human health and contribute to the climate crisis. In addition, there are bottom-up movements emanating from the population to make healthier coatings from biobased sources as well as difficulties securing supplies due to the pandemic and obtaining specific chemical structures from petrochemical sources. While these reasons certainly encourage the coating industry to transition towards greener, safer, and more locally sourced coating solutions, implementing new regulations remains one of the most effective ways to transform the industry. Such regulations are necessary to ensure that the ambitious GHG emission reduction targets are met [3].



Fig. 1 Illustration of the concept of circular economy

VOC regulations have been tightened considerably in recent decades in most parts of the world. Limit values have been established for liquid coatings ("in-can" limits) and for finished goods. As an example, Table 1 presents the limit values for different volatile substances in wood-based furniture. Values differ significantly from one region/country to another. To meet these limits, the use of water-based and UV-curable coatings, which has grown considerably in recent decades in the wood industry, is necessary. However, considering that VOCs are not the sole contributor to GHG emissions in the coatings industry, transitioning towards responsible sourcing (using biobased products, reusing, and recycling) is of utmost importance.

Biocides are also strongly regulated and have been subject to increasingly tighter restrictions over the last few years; for example, the Biocidal Products Regulation (BPR, Regulation (EU) 528/2012) which ensures that commercialized biocidal products marketed in the EU offer a high level of protection for humans and the environment [5]. The incan preservatives that paint manufacturers have traditionally used to control paint spoilage include isothiazolinone, formaldehyde releasers, and halogenated compounds. On the other hand, the most widely used wood preservatives that prevent wood degradation (by fungi, rot, decay, termites, mold, etc.) are water-soluble preservatives, such as alkaline copper quaternary (ACQ-B, ACQ-D), copper azole (CA), and micronized copper azole (MCA). New regulations are restricting traditional biocides and preservative usages, among other things, by reducing the availability of biocides for in-can preservation. However, they are also pushing product development towards more sustainable and less toxic solutions.

In addition to the regulations that set the rules and thresholds to be followed, life cycle analysis (LCA) [1, 2] helps to justify and guide technological choices. In Europe, the ISO 14040 standard pertaining to buildings has been clarified by the EN 15804 standard [3]. There is also an international version of this standard, the ISO 21930. [4]. Life cycle analysis makes it possible, among other things, to avoid the displacement of pollution from one life cycle phase to another and from one environmental impact to another. The problem of wood surface treatment based on biosourced substances could be justified by the LCA, particularly the impact of VOCs. However, there are very few LCA studies on wood coatings. We can note the work of Montazeri and Eckelman, who studied the impact of replacing 50% of a wood flooring coating by a bio-renewable content (BRC) [10]. Comparative results showed greater than a 30% reduction in six out of ten impact categories. Still, the impact on the four other categories (smog formation, eutrophication, acidification, and respiratory effects) were more important. These results show that not only the percentage of bio-sourced content

Table 1         Limit values for different volatile substand	es [4]	
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Regulation-country	Substances	Limit values
Germany	Carcinogenic compounds (3 days)	0.01 mg/m <sup>3</sup>
	TVOCs (3 days)	$10 \text{ mg/m}^3$
	Carcinogenic compounds (28 days)	0.001 mg/m <sup>3</sup>
	TVOCs (28 days)	$1 \text{ mg/m}^3$
Belgium	Formaldehyde (28 days)	0.1 mg/m <sup>3</sup>
	Acetaldehyde (28 days)	$0.2 \text{ mg/m}^3$
	Toluene (28 days)	0.3 mg/m <sup>3</sup>
	TVOCs (28 days)	0.1 mg/m <sup>3</sup>
	Carcinogen substances	0.001 mg/m <sup>3</sup>
RAL UZ38 (Northern Europe)	Formaldehyde	0.05 mg/m <sup>3</sup>
	Organic compounds with a boiling point between 50 $^\circ$ C and 250 $^\circ$ C	600 µg/m <sup>3</sup>
	Organic compounds with a boiling point higher than 250 °C	100 µg/m <sup>3</sup>
	CMR (carcinogenic, mutagenic, reprotoxic)	$< 1 \ \mu g/m^{3}$
China	Formaldehyde emission	$\leq$ 0.10 mg/m <sup>3</sup>
	Benzene	$\leq$ 0.11 mg/m <sup>3</sup>
	Toluene	$\leq$ 0.20 mg/m <sup>3</sup>
	Xylene	$\leq$ 0.20 mg/m <sup>3</sup>
	TVOC	$\leq$ 0.60 mg/m <sup>3</sup>
ANSI/BIFMA X7.1–2011 (R2016) (USA)	TVOC	$\leq$ 0.50 mg/m <sup>3</sup>
	Formaldehyde	$\leq$ 50 ppb
	Toluene (28 days)	$\leq$ 25 ppb
	Total aldehyde	100 ppb

TVOC\* total volatile organic compound

should be considered when formulating bio-based products, but rather multi-environmental goals [11].

Other studies show that increasing the lifetime of coatings is emerging as one of the most efficient strategies to limit the environmental impact of coatings [12, 13]. As such, studies describing performance enhancement of wood coatings remain of great importance.

### Replacement of Petroleum-Based Chemicals in Coating Formulations

The development of biobased and recycled coatings aims to reduce the use of petroleum-based raw materials. To date, there is no minimum percentage of biobased raw material required to obtain or use the designation "biobased coating" in most countries. However, some countries and regions have enacted laws governing the designation so consumers can better understand and appreciate the products they use. In Switzerland, for instance, a label called *Umweltetikette*, meaning "environmental label," identifies products made of renewable raw materials. It can be affixed to paints, varnishes, glues, and wood preservatives and aims to facilitate the selection of environmentally friendly products. The label's main requirements are 95% renewable raw materials and minimum performance levels [14••].

Increasing the amount of biobased or recycled content in coatings can be achieved by using them in place of petroleum-based resins, liquid carriers, fillers, and additives. It is generally accepted that the raw materials used in the coatings industry should not compete with human or animal food and that locally sourced raw materials should be preferred. Without strict regulations, in most countries, biobased or recycled coatings must perform as well as or better than their petroleum-based counterparts or sell at a lower price to enter the market.

#### **Revalorization of Paint and Coating Performance**

Recycling and reusing waste paint offer ways to render the paint industry more sustainable by conserving resources and energy and reducing the amount of waste paint ending up in landfills, as Americans alone discard over 65 million gallons of paint each year [15]. Companies now offer lower-quality recycled paints at a lower cost [16, 17]. While companies offer different recycled latex paints for interior and exterior applications, the choice is often limited to opaque premixed color paints. Recycled finishes for wood applications are

very limited, and, to our knowledge, very few studies report on the performance of recycled coatings on wood.

Progress has been made in the use of recycled compounds in paints. These paints can be formulated, for instance, by using pigments recovered from paint waste in place of pigments from virgin raw materials [17]. Research also focuses on ways to recover raw materials, such as resin, from paints for reprocessing into new products. Acrylic resins are the most widely used binder in wood coatings today [18]. Global demand for acrylic resins exceeded 1.3 million tons in 2020 and is expected to increase [19]. A Japanese company has built a pilot plant in Japan to chemically recycle acrylic resins such as poly(methyl methacrylate). Products from recycled methyl methacrylate monomer should be available in the spring of 2023. While recycled paints might not gain significant market share for applications where performance or appearance is crucial, they could be of interest for less demanding applications.

#### Use of Biobased Compounds in Coating Development

Various biosourced molecules from animal and plant sources have been the subject of many studies aiming to incorporate them into coatings. As we explain in this section, they can be used as resin replacements, as well as additives, fillers, and liquid carriers.

#### **Biopolymers as Film Formers**

Lignin, chitin/chitosan, and proteins are the biopolymers that have been the most studied as resin replacers in different sectors (adhesives, coatings, etc.) and show the most significant potential for that purpose.

Lignin Lignin shows great potential to be used as a raw material in biobased coatings and other materials due to its aromatic structure, thermal stability, and biodegradability. It is one of the three main constituents of lignocellulosic biomass, the other two being cellulose and hemicellulose, and the aromatic polymer that is most abundant in nature. The wood processing industries have estimated that 50 billion tons of lignin is produced per year worldwide, while only 2-5% is used to produce biomaterials [20, 21]. Lignin is an amorphous molecule that contains three phenylpropane units: p-hydroxyphenylpropane (H), guaiacylepropane (G), and syringylpropane (S) [20]. It represents about 20-30% of the total mass of wood and is also present in high quantities (roughly 30.5%) in the bark of trees [22]. It can be extracted from wood using kraft pulping, sulfite, soda, Organosoly, and several other processes [23]. Its structure, solubility, molecular weight, hydroxyl groups, and purity differ depending on the extraction process used. The potential applications for lignin depend strongly on its properties [20].

In recent years, lignin has been used to prepare various coatings, especially polyurethanes (PUs), epoxies, and UVcurable coatings. It has been used as extracted from wood, or other materials, fractionated to obtain low molecular weight fractions (e.g., vanillic acid) or modified to enhance its reactivity (e.g., by adding hydroxyl groups) [24•]. Studies on PU report lignin being used to partially or totally replace the polvol component or modified to be used in place of the polyisocyanate hardener [25, 26]. A study led by Wang et al. (2020) showed it is possible to replace fossil-based polyol with lignin to form flame-retardant PU. Lignin's aromatic structure contributes to the formation of a dense carbon layer in the PU matrix that acts as a barrier to prevent the release of combustible gases and block oxygen, which reduces the flame rate [25]. The limiting oxygen index was found to increase with the amount of lignin used. De Haro et al. (2019) showed that a lignin-derived biobased diisocyanate used with different technical lignins, such as polyols, represents an interesting route to produce thermoset PU coatings with high biomass content [24•]. However, it has also been shown that PU formulations with a high percentage of lignin can crack and become more permeable than their petrochemical counterparts. Adding low-surface-tension film-forming agents would be a viable solution to counteract cracking [27]. While lignin has shown great potential to increase the amount of biobased content in PU coatings, its low solubility and reactivity, high glass transition temperature (Tg) and polydispersity, the propensity to photodegrade, and dark color continue to represent challenges for its use. More research is needed to tackle these issues and enable the widespread incorporation of lignin in PUs.

While using biobased isocyanates instead of petroleumbased ones makes it possible to increase the amount of biobased content in coatings, isocyanates remain problematic as they are associated with health and safety issues. Isocyanates react with polyols by condensation polymerization to form polyurethanes. Health and safety issues related to isocyanates can be avoided by preparing isocyanate-free PUs, which are becoming more popular nowadays. Isocyanate-free PUs can be synthesized in two ways: a transurethanization reaction and the nucleophilic addition of diamine to cyclo-carbonate (Fig. 2A and B). The latter approach is getting more attention as it is performed under mild reaction conditions with readily available raw materials. This technology is expected to continue growing in popularity over the next few years.

#### Polysaccharides

Polysaccharides such as cellulose, starch, and chitosan from chitin are commonly studied as polymer films and coatings for food packaging because of their sustainability,



Fig. 2 Reactions of formation of isocyanate-free urethane moieties through transurethanization (A) and nucleophilic addition between diamine and cyclo-carbonate (B)

accessibility, low cost, and antibacterial properties [28, 29]. Chitin is a polysaccharide composed of N-acetylated glucosamine repeat units and is the second most abundant polysaccharide on earth after cellulose. It can be extracted from the skeleton of shellfish (crab, lobster, shrimp). Chitosan is obtained by deacetylating chitin to obtain a linear polymer made of glucosamine and N-acetylglucosamine units [30]. Chitosan has been used with dopamine hydroxyapatite to create a layer-by-layer (LBL) coating on beech (Fagus orientalis Lipsky) wood. The LBL coating increases the wood's hydrophobicity and delays its degradation in seawater [31]. In another study, medium molecular weight (MW) chitosan (1-10% concentration) and a chitosan oligomer (1-3% concentration) were evaluated as water-based wood coatings to protect poplar (Populus L.) wood against white rot fungus (T. versicolor) mycelia. The authors observed that the medium MW chitosan was more protective than the chitosan oligomer. They hypothesized this was due to its higher viscosity and adhesion properties [32]. Finally, Andok et al. (2021) studied the effect of chitin deacetylation reaction times on chitosan-based coatings [33]. They noted that the longer deacetylation takes, the lower the coating's viscosity and the shorter its drying time. However, no effect on water absorption was observed.

**Proteins** Proteins are composed of amino acids. They can be separated into three main categories: vegetable proteins such as soy proteins, gluten, and zein; animal proteins such as collagen and gelatin; and dairy proteins such as whey proteins and caseins [34]. Soy and dairy proteins have been the most studied for wood finishes and adhesives.

Researchers are increasingly considering soy proteins because of their low cost and biodegradability. One of the latest developments related to protein addition is the mechanical performance improvement of water-based polyacrylic coatings [35]. The coatings were modified by graft copolymerizing a soy protein isolate containing up to 90% protein. This process increased the wear and scratch resistance of the coating. In addition, the graft density increased as the soy protein isolate content increased, leading to an increase in the tensile strength and elastic modulus [35].

Proteins have also been studied to improve the fire resistance of wood coatings. Proteins-mostly casein-are increasingly being studied as flame retardants because they ensure superior thermal stability and produce less toxic smoke than phosphorus-based flame retardants due to their high phosphorus and nitrogen content [34, 36]. Flame-retardant proteins are made of serine and arginine with high nitrogen content (17.4%) and alpha-casein proteins with high phosphorus content (7.22%) [37]. One way to prepare such coatings is to form a casein-magnesium composite as an intumescent fire-retardant coating for pine (Pinus radiata D.Don) wood. Casein is a protein that makes up most of the nitrogenous component of milk. Thermogravimetric analysis has proven that casein-magnesium composites can produce magnesium oxide, a thermally stable insulator [38]. However, the durability of protein-based flame retardants remains a concern. Research has shown that it is possible to improve the durability and flame retardancy of protein coatings by fusing mussel foot protein-5 (mfp-5) adhesion domain with flame-retardant proteins. Finally, casein can also be used as a surfactant in biobased latexes [39], and these latexes could be employed in the formulation of waterborne coatings for wood.

While several studies have reported the potential of proteins in wood coatings, this area needs to be further developed. More fundamental studies are required to understand the impact of amino acids on the resulting coating's adhesion properties and of the molecular weight and structure of proteins on the coating's properties.

**Oils** Oils are triglycerides that contain different fatty acids and are characterized by the number of unsaturations they contain. They were among the first chemicals used to protect wood. Drying oils (penetrating finishes) can be applied and dried on wood surfaces. Oils can also be used to synthesize alkyds. They are still used nowadays due to their availability, low cost, and hydrophobicity, the latter of which sets them apart from most biobased polymers. In recent years, oils have been used to increase the biobased content of Pus [40, 41], epoxies, and photopolymerizable coatings. Linseed and castor oils are the most widely used, but other region- or process-specific oils (e.g., pyrolysis bio-oil) have also been used. Oils can be modified through different chemical reactions (thiol-ene coupling, ozonolysis, hydroformylation, photochemical oxidation, and epoxidation) to be used as polyols. Epoxidized and acrylated oils can also be prepared and used in UV-curable formulations. Furthermore, acrylated oils can be used to prepare acrylic latexes [42]. Finally, oils can be modified and used as biobased isocyanates [43].

#### Additives

Up until a couple of years ago, the additives used in coatings and finishing products originated mainly from petroleum derivatives (e.g., waxes) or were mineral-based (e.g., silica  $(SiO_2)$ , titanium oxide  $(TiO_2)$ , clay). Sustainable compounds—specifically biopolymer additives—can be added instead to improve coatings' properties. The section below describes the potential of such additives.

Nanocellulose Nanocellulose term refers to nanostructured cellulose, which includes nanocrystalline cellulose (NCC), nanofibrillated cellulose (NFC), also known as microfibrils cellulose, and bacterial nanocellulose (BC). Nanocellulose has a regular, highly ordered nanostructure. It shows interesting potential as an additive because of its stiffness, low density, insulating properties, mechanical properties, and dimensional stability [44]. It has been studied as an additive in coatings, latex paint, and foams to improve their mechanical and thermal properties [45••]. Various studies report using nanocellulose to improve mechanical properties. Pacheco et al. (2021) evaluated the incorporation of nanocellulose, TiO<sub>2</sub>, and SiO<sub>2</sub> in an acrylic varnish [46]. The authors demonstrated that adding NCC enhanced the varnish's surface mechanical properties while maintaining its aesthetical. Similar results were reported by Hochma'nska-Kaniewska et al. (2022), who applied an acrylic coating containing 1% NCC to pine (Pinus radiata D.Don) and beech (Fagus sylvatica L.) wood [47]. Their study showed the wood's abrasion resistance and impact resistance improved. Chemical grafting can also be used to formulate water-based PU with NCC. This method has been shown to improve the coating's tensile strength, elongation at break, hardness, and abrasion resistance with only 0.1% NCC [48]. Moreover, nanocellulose modification to enhance the antimicrobial and fungi resistance of coatings has been evaluated in several studies, which are summarized in a review by Norrahim et al. (2021) [49].

MFC can also be used as additives in coatings. They differ from NCC in terms of their fiber size distribution, with MFC fibers being narrower and longer than NCC [50]. They are obtained by a mechanical process that does not require chemicals or enzymes. Kluge et al. (2017) reported a considerable increase in strength and stiffness when using 2% MFC in a water-based wood varnish [51]. More recently, MFC was used as a rheology modifier in a water-based exterior coating. The formulation displayed increased mud crack resistance during curing and excellent sag resistance [52].

Although nanocellulose is more expensive to produce than MFC, NCC has been more extensively studied and seems to have more potential as an additive in wood coatings. Moreover, there are already companies that can produce several tons of nanocellulose per year [53]. Several projects are underway to reduce the cost and environmental impact of NCC extraction processes.

**Chitin/Chitosan** Although chitosan (Fig. 3) has been used as a film-forming agent, it can also be used as an additive (as fibers, microspheres/microparticles, nanoparticles) in wood coatings. The interaction between caffeine and chitin has also been studied for biocidal wood coating [54]. The authors of that study observed the interaction between the two molecules by spectrometric analysis. They confirmed that chitin and caffeine could bond with beech (*Fagus sylvatica* L.) wood. In another study, chitosan, ammonium polyphosphate, and montmorillonite were mixed and coated with melamine formaldehyde to obtain a biobased flame-retardant additive for waterborne epoxy resin. The authors showed that the resin coating was water resistant, and its flame-retardant efficiency could be explained by an expanded and integrated char layer on the wood surface [55].

Although chitosan incorporation has progressed significantly over the last few years, new ecological extraction methods are needed (and are in development) to ensure chitosan-based coating solutions have a low environmental impact [56].

**Lignin** The increasing demand for UV absorbers with minimal environmental impact while providing high protection has prompted the development of UV absorbers from natural organic resources [57–59]. Lignin is a biomass resource that



Fig. 3 Chemical structure of chitosan

can, due to its chromophore groups, be used in the UV protection of polymers. This resource has therefore been fully investigated in the literature. Indeed, it has been proven that the low molecular weight lignin fraction shows better UV protection than untreated lignin [59]. This protection improvement is also observable when using lignin in microparticles and nanoparticles forms. Another study showed that colloidal lignin formation, using Organosolv lignin from pine wood prepared as nano-colloidal particles, provides better protection and photostability than the original raw lignin [59]. However, lignins impart an undesirable dark color to UV protection products. This dark color could be minimized by using lignin nanoparticles rather than microparticles [58].

Biobased Biocides and Preservatives There has been an increase in the number of research studies on the feasibility of using biobased biocides and preservatives to produce new effective solutions for sustainable wood protection. One can see a simple solution for environmentally friendly wood protection lies in using natural products such as essential oils [15, 60, 61], caffeine [62], tannins [14••, 63–65], resins [66], and chitosan [32]. However, these natural products are not yet used on an industrial scale due to their limited range of protection against biological agents and weathering, leaching, their high cost, and variability in their chemical composition  $[67 \bullet \bullet]$ . There are also emerging technologies in the area of biobased preservatives. However, they have mainly been studied in the food and pharmaceutical industries and have yet to be investigated in the wood coatings industry. Recent trends include engineered enzymes and antimicrobial peptides (AMPs). Hodges et al. (2018) reported that the synergistic effect between enzymes (glucose oxidase and lysozomes) and 2-methyl-4-isothiazolin-3-one (MIT) in a conventional paint led to the decrease of MIT concentration needed to achieve similar performances [68]. AMPs usually comprise 6 or 7 amino acids and are antimicrobially effective against bacteria, fungi and viruses. Furthermore, it is possible to use them in liquid and dry film coatings. McDaniel et al. tested AMP-6 and AMP-7 in polyvinyl alcohol (PVA) and reported that AMPs could facilitate the activity of traditional biocides like MIT and made it possible to use fewer biocides [69]. Challenges such as achieving the same performance as traditional preservatives at a similar or lower cost and the long and expensive homologation processes make it difficult for new products to achieve commercialization.

**Other Additives and Fillers** Most of the fillers used in coating formulations are mineral based. While most of them do not present significant health and safety concerns in coating formulations, their extraction and production are often very polluting [70]. It is possible to valorize different agricultural by-products, such as fruit pits and shells, to prepare powders that do not interfere with the food chain. For example,

silane-coated olive pit powder has been developed and used to increase the surface hardness and scratch and impact resistance of coatings [71]. Almond, walnut, and pistachio shells and peach, apricot, and avocado stones have also been shown to have potential as coating fillers to replace liquid plastics, silica, wax, and other micro-granules. In addition to being sustainable (producing zero emissions during manufacturing) alternatives to the additives previously mentioned and being odorless, they have also been shown to improve coatings' resistance to abrasion (3.5 Mohs scale hardness) and slip resistance (when used in floor coatings). Although these solutions are very interesting from an environmental point of view, their production is region-specific. Nevertheless, they are a good example of how residues from the food industry can be valued. Drawing inspiration from this work to manufacture additives is an interesting avenue to promote the local economy.

#### **Biobased Liquid Carriers**

While most advancements in coating development over the last few years have focused on water-based and photopolymerizable coatings, the development, promotion, and use of biobased solvents are also expanding, as these solvents can be used to reduce the VOC emissions of coatings that are solvent-based or contain solvents. Methyl soyate and other soy methyl esters (from soybeans), ethyl lactate (formed from lactic acid and ethanol, which is made from processing corn or from the catalytic depolymerization of post-consumer polylactic acid [72, 73], and D-limonene (citrus rind oil) are a few examples of biobased solvents [74]. The main advantages of coatings formulated from such solvents are reduced toxicity, biodegradability, reduced VOC emissions, and increased worker safety and environmental friendliness [75]. While several studies have focused on the development or sustainable extraction of such solvents, few studies report on their performance in coatings compared to that of their petroleum-based counterparts.

#### Smart and Functional Coatings

The advent of stimuli-sensitive coatings offers the potential to decrease the EI of coatings and limit the use of toxic chemicals. They can extend the life of coatings by integrating self-healing functions or offering multifunctional protection, sanitize the air in buildings by absorbing and degrading pollutants, or limit heating/conditioning by filtering parts of the electromagnetic spectrum. Stimuli-sensitive coatings also offer the potential of using substrates, such as wood, in broader conditions by conferring them new properties. While the first generation of stimuli-sensitive coatings was essentially based on petroleum-based raw materials, their development is now transitioning towards biobased raw materials. The following section details recent advances in stimuli-sensitive and functional coatings for wood substrates.

#### **Self-Healing Coatings**

Adding self-healing properties to wood coatings is a promising way to improve their sustainability. Over their lifetime, wood coatings must face mechanical aggression, particularly when they are applied on wood flooring and tables. Even if a coating has improved mechanical properties, scratches can still occur, which subsequently reduce the coating's ability to protect the substrate, making the item in question less aesthetically pleasing.

Self-healing materials can be achieved using two main approaches. The first way is the extrinsic approach, and involves dispersing microcapsules containing a healing agent in the coating [76]. Under stress, the capsules break and release the healing agent, which flows into the crack and repairs it after curing [76] (see Fig. 4). This strategy enables autonomous healing to repair large volumes; however, since the capsules cannot be refilled, it can occur only once. Moreover, the mechanical properties of the capsules must be tuned to break only at the right moment, not during the coating application process. Their size and number must also be controlled to ensure coating transparency and mechanical and aging resistance and to minimize sensitivity to liquid [77]. In 2021, Yan et al. developed microcapsules that had a mix of acrylic and shellac resins as their core and a melamine-formaldehyde resin shell [77]. The authors used them in a waterborne acrylic primer for European lime (Tilia europaea L.). They observed that the width of a 16 mm scratch was reduced by 39%. Later, they developed another system with microcapsules having cellulose and urea-formaldehyde resin shell and a tung oil core; however, it self-healed less effectively [78].

The second way is the intrinsic approach, which is usually based on reversible intermolecular interactions that enable broken bonds to be repaired and induce repeatable healing (Fig. 5). Depending on the material and interactions chosen, heat may be necessary to trigger the healing process by increasing the mobility of the polymer chains and dissociating the reversible bonds. Many self-healing materials have been developed using reversible C-C bonds [79], S–S bonds [80], and H-bonds [81]. H-bonds have been more widely explored for wooden substrates due to their low selfhealing temperature [82]. In 2020, Paquet et al. studied the self-healing properties of UV-cured polyacrylate coatings for wood finishing systems [82]. They demonstrated that H-bonds introduced in a coating through alcohol-bearing monomers could make scratches disappear entirely after 2 h of heating at 80 °C. Later, Sun et al. used H-bonds in a poly(vinyl alcohol) network to give a fire-retardant waterbased plywood coating self-healing properties [83]. Selfhealing was observed after placing the coating under water vapor for several minutes and then leaving it at ambient temperature for 30 min. Zhang et al. developed a gelatin-based biodegradable fire-retardant bio-gel coating for wooden construction [84]. Due to the numerous H-bonds in the gel and the flexibility of the network, cracks could be repaired after heating at 60 °C for 70 s. In 2014, a nanotech company developed and commercialized a self-healing solvent-based 2K PU coating suitable for wood [85]. The self-healing properties were made possible by a flexible thermoplastic polymer phase, while a thermoset polymer phase ensured good mechanical properties.

Numerous challenges remain for self-healing wood coatings. Depending on their intended applications, many constraints must be considered, such as their Tg, mechanical properties, aging properties, transparency, color, and cost effectiveness. The self-healing strategy used must consequently be chosen wisely to suit those requirements. To date,



Fig.4 Extrinsic self-healing process with microcapsules filled with healing agent



Fig. 5 Intrinsic self-healing process based on reversible interactions

most capsules designed especially for wood coatings are derived from formaldehyde, which is toxic and increasingly regulated in the coatings industry, and none enable complete healing. Further research is needed to improve their healing performance and to replace urea–formaldehyde resins as a shell material. Intrinsic healing strategies perform better but are generally closely tied to coating softness and usually require heating to trigger the self-healing process. It could be interesting to study different heating sources to determine which is most efficient in a real-life situation. Moreover, more effort could be devoted to further improving the sustainability of self-healing coatings for wood, notably by incorporating biobased polymers in the coatings.

#### **Flame-Retardant and Fireproof coatings**

A lot of research is currently underway to develop flameretardant (FR) and fireproof (FP) coatings that are wellsuited to wood substrates in terms of their transparency and resistance to water and humidity). FR coatings generally prevent flame spread and protect wood furniture and textiles, whereas FP coatings also prevent fire ignition and spread. In the last 5 years, biobased FR coatings have been a topic of great interest in wood science.

Chitosan is considered an interesting additive for these types of coatings. Its efficiency as a component in intumescent coatings has been studied since it is rich in carbon and releases nitrogen gas as it degrades. Cho et al. (2022) reported that wood samples coated with ion-complex hypophosphorus-crosslinked chitosan produced more char residue and exhibited better self-extinguishing behavior than uncoated wood [86]. Rao et al. (2019) mixed chitosan (10%), ammonium polyphosphate (APP) (30%), and silica nanoparticles at different ratios (0-4%) in a PU resin [87]. Their results showed the biocomposite coating was a better flameretardant with the addition of silica nanoparticles. LBL is another way in which biobased coatings can be prepared. Zhou et al. (2020) studied balsa (Ochroma pyramidale (Cav. ex Lam.) Urb.) wood covered with an LBL coating prepared using chitosan, sodium phytate, and TiO<sub>2</sub>-ZnO nanoparticles [88]. More recently, Yan et al. (2022) prepared a durable FR coating for wood using an LBL self-assembly approach, chitosan, graphene oxide, and APP [89]. These studies have demonstrated that LBL coatings applied to wood can decrease the wood's initial and maximum thermal decomposition temperature while significantly increasing the char residue.

In another study, soy oil was used to synthesize a phosphorus-containing FR diallyl 4-phenylphosphonicbenzoic (DAPB) via UV-assisted radical polymerization to form a soy oil-based coating resin. The resulting coating was transparent, halogen-free, FR, and exhibited good adhesion properties [90]. Moreover, a group of researchers prepared a multifunctional castor oil-based UV-cured FR coating containing phosphorus, silica, and sulfur by thiol-ene click reaction and applied it to wood surfaces. The coating exhibited improved pencil hardness and adhesion due to the addition of trimethyl-2,4,6-trivinylcyclotrisilazane (TTC). They also proved that their coating inhibited heat and oxygen transfer and prevented the wood substrate from burning by developing a barrier char [91].

As previously mentioned, proteins have also been studied for their ability to produce fire-retardant biobased coatings. For example, Uddin et al. (2020) mixed casein with magnesium hydroxide to obtain an intumescent FR coating [38]. Molecules from lignin and wood extractives like tannins have also been studied as additives for biobased FR coatings. In one study, tannins were used as FR compounds in a water-based acrylic coating with microcapsules of monoammonium phosphate. The authors observed the coating had a better carbonization index than commercial coatings but was less adhesive due to clumping and the flexibility of the film [92]. In another study, high MW tannins extracted from pine (Pinus radiata D.Don) were used to produce a dual active-passive coating with intumescent and FR properties. The coating developed FR properties with carbonaceous layer formation at a high tannin concentration (13%), whereas it exhibited more intumescent properties with a carbonaceous foam layer at a low concentration (2.5%) [93•]. Yet other authors have mixed tannic acid [94] and modified vanillin from lignin [95] with different types of epoxy resin to evaluate the potential of these new biobased FR coatings. Finally, as cited before, modified oils have the advantage of being non-toxic, not emitting VOCs, and being able to be used as film formers for coatings.

#### Superhydrophobic and Self-Cleaning Coatings

Superhydrophobic wood coatings have received a lot of attention in recent years. However, they typically contain fluorinated materials that can be toxic. Biobased polymers, silicon-based, and fluorine-free coatings are seen as promising sustainable alternatives to superhydrophobic wood coatings [96]. Siloxane polymers such as vinyl terminated polydimethylsiloxane and poly(methyl hydrogen siloxane) [97], and polydimethylsiloxane (PDMS) have been tested for their superhydrophobic properties [98-100]. Some siloxanes, such as tetraethylorthosilanes, have also been studied in combination with two biobased polymers (hydroxyethyl cellulose (HEC) and hydroxyethyl starch (HES)) [101]. Researchers have also investigated other combinations, such as 3-mercaptopropytriethoxysilane and octadecyltrichlorosilane with nano-Al<sub>2</sub>O<sub>3</sub> and polydopamine [102] and siloxane polymers with castor oil [103]. All these studies reported the coated surfaces had very high water contact angles between 150 and 165°. However, the siloxane coatings, despite being

reported as *environmentally friendly biobased superhydrophobic coatings*, still use solvents such as toluene, tetrahydrofuran, and cyclohexane, which are volatile and toxic, and decrease their sustainability.

Other studies have evaluated more eco-friendly ways to produce superhydrophobic coatings. For example, in one study, alkyl ketene dimer wax microparticles were spraydeposited on beech (Fagus sylvatica L.) to coat its surface. The authors determined the coating's water contact angle to be 160°, and it decreased to 125° after prolonged rubbing because shear forces destroyed the wax microstructure. The authors proved that thermal treatment applied at 80° to the damaged surface renews the wax microstructure and makes it possible to recover the original high water contact angle [104, 105]. A review written by Saji et al. (2020) summarizes the research that has been done on wax superhydrophobic coatings [106]. They reported that tung oil and beeswax can be mixed and applied to spruce (Picea spp.). The best formulation was 1 part wax to 5 parts tung oil, with micronized sodium chloride particles, which achieved a water contact angle of 160° [107]. Although sustainable superhydrophobic coatings have the potential to be used on wood, they are not yet commercially available.

#### Conclusion

This review presents several advances that have been made, as well as key trends in the wood coatings industry. As the industry continues to look for low-VOC coating solutions, it is also seeking to source components more sustainably. Coating producers still face challenges regarding the availability and quality of biobased raw materials and balancing performance versus cost. Financial incentives from governments or other regulatory agencies could help increase the use of biobased raw materials, which will help to optimize processes and, down the line, reduce the cost of biobased materials.

The development of smart functional wood coatings is growing quickly, and many efforts are devoted to increase their sustainability with safe alternatives.

While most of the sustainable coating solutions discussed in this review focus on well-known and widely accepted coating chemistries and technologies (water-based and photopolymerizable PUs, acrylics, and epoxies), new technologies that are expected to gain more importance over the next few years are also presented (LBL, polyelectrolyte complexes, isocyanate-free PU).

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#### Declarations

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#### References

Papers of particular interest, published recently, have been highlighted as:

- Of importance
- •• Of major importance
- Wood LG. Well-being and performance: the human and organizational benefits of wood buildings [Internet]. Forestry Innovat Invest. 2020. Available from: https://www.naturallywood.com/ wp-content/uploads/wood-well-being-and-performance\_report\_ graham-lowe.pdf. Accessed 2 Aug 2023.
- 2. Anastas P, Eghbali N. Green chemistry: principles and practice. Chem Soc Rev. 2010;39:301–12.
- Challener C. An update on sustainability in the coatings industry. JCT CoatTech. 2018;15:22–8.
- 4. Ulker OC, Ulker O, Hiziroglu S. Volatile organic compounds (VOCs) emitted from coated furniture units. Coatings Mdpi. 2021;11:806.
- Centre (JRC) ECA (ECHA) and EFSA (EFSA) with the technical support of the JR, Andersson N, Arena M, Auteri D, Barmaz S, Grignard E, et al. Guidance for the identification of endocrine disruptors in the context of Regulations (EU) No 528/2012 and (EC) No 1107/2009. EFSA J. 2012;16:e05311 Wiley Online Library.
- Finkbeiner M, Inaba A, Tan R, Christiansen K, Klüppel H-J. The new international standards for life cycle assessment: ISO 14040 and ISO 14044. Int J Life Cycle Assess. 2006;11:80–5.
- ISO E. 14044: Environmental management, life cycle assessment, requirements and guidelines [Internet], DIN Deutsches Institut f
  ür Normung e. V. Beuth Verlag, Berlin; 2006. Available from: https://www.iso.org/fr/standard/38498.html. Accessed 2 Aug 2023.
- EN 15804:2012+A2:2019 Sustainability of construction works-Environmental product declarations - Core rules for the product category of construction products [Internet]. iTeh Standards. Available from: https://standards.iteh.ai/catalog/stand

ards/cen/c98127b4-8dc2-48a4-9338-3e1366b16669/en-15804-2012a2-2019. Accessed 29 Apr 2023.

- ISO I. 21930: 2017-Sustainability in buildings and civil engineering works-core rules for environmental product declarations of construction products and services [Internet]. Geneva (Switzerland): International Organization for Standardization. 2017. Available from: https://www.iso.org/standard/61694. html. Accessed 2 Aug 2023.
- Montazeri M, Eckelman MJ. Life cycle assessment of UV-curable bio-based wood flooring coatings. J Clean Prod Elsevier. 2018;192:932–9.
- Schmidt JH, Christensen P, Christensen TS. Assessing the land use implications of biodiesel use from an LCA perspective. J Land Use Sci Taylor Francis. 2009;4:35–52.
- 12. Life-cycle assessment of architectural coatings [Internet]. American Coatings Association. [cited 2023 May 1]. Available from: https://www.paint.org/coatingstech-magazine/articles/life-cycleassessment-of-architectural-coatings/
- Strömberg L. Integrated life-cycle design of coatings on exterior wood: part 2: life-cycle assessment. Surface Coat Int Part B-Coat Trans. 2004;87(3):211–20.
- 14.•• Gesthusien. Bio-based coatings overview: increasing activities [Internet]. European Coatings. 2020. Available from: https:// www.european-coatings.com/articles/archiv/bio\_based-coati ngs-overview-increasing-activities. Accessed 6 Oct 2022. This reference explains the steps taken by some countries to encourage the use of biosourced and recycled raw materials to design coatings
- Antonelli F, Bartolini M, Plissonnier M-L, Esposito A, Galotta G, Ricci S, et al. Essential oils as alternative biocides for the preservation of waterlogged archaeological wood. Microorganisms MDPI. 2020;8:2015.
- Huard L, Muehlethaler C. Recycled paints: are they as variable as they seem? Forensic Science International. Elsevier. 2022;340:111476.
- Karlsson MC, Álvarez-Asencio R, Bordes R, Larsson A, Taylor P, Steenari B-M. Characterization of paint formulated using secondary TiO2 pigments recovered from waste paint. J Coat Technol Res Springer. 2019;16:607–14.
- Poth, Schwalm, Schwartz. Acrylic Resin [Internet]. European Coatings Tech Files. 2011. Available from: https://docplayer.net/ 142410641-European-coatings-tech-filesu-poth-r-schwalm-mschwartz-acrylic-resins-ebook.html. Accessed 2 Aug 2013.
- Rais A. Sumitomo chemical to build pilot plant for chemical recycling of PMMA [Internet]. Process Worldwide. 2021. Available from: https://www.processworldwide.com/sumitomo-chemi cal-to-build-pilot-plant-for-chemical-recycling-of-pmma-a-1051090/. Accessed 29 Apr 2023
- Ridho MR, Agustiany EA, Rahmi Dn M, Madyaratri EW, Ghozali M, Restu WK, et al. Lignin as green filler in polymer composites: development methods, characteristics, and potential applications. Adv Mater Sci Eng. 2022;2022:1363481.
- Demuner IF, Colodette JL, Demuner AJ, Jardim CM. Biorefinery review: wide-reaching products through kraft lignin. BioResources. 2019;14:7543–81.
- Liu L-Y, Patankar SC, Chandra RP, Sathitsuksanoh N, Saddler JN, Renneckar S. Valorization of bark using ethanol–water organosolv treatment: isolation and characterization of crude lignin. ACS Sustain Chem Eng ACS Publ. 2020;8:4745–54.
- 23. Tribot A. Valorisation de la "partie lignine" des effluents de prétraitement de biomasse forestière : élaboration et caractérisation d'agrocomposites [Thesis, Internet]. Université Clermont Auvergne; 2020. Available from: https://theses.hal.science/tel-03048262v2. Accessed 2 Aug 2023.
- 24.• de Haro JC, Allegretti C, Smit AT, Turri S, D'Arrigo P, Griffini G. Biobased polyurethane coatings with high biomass content:

tailored properties by lignin selection. ACS Sustain Chem Eng ACS Publ. 2019;7:11700–11. This study shows that the design of PU coatings, based on different technical non-chemically modified lignins, is a promising strategy for the development of high-performance thermoset systems. It is also mentioned that the physicochemical properties of PU coatings can be adjusted according to the lignin precursor used, thus opening the way to the production of biobased PU coatings with customized characteristics.

- 25. Wang Y, Zhang Y, Liu B, Zhao Q, Qi Y, Wang Y, et al. A novel phosphorus-containing lignin-based flame retardant and its application in polyurethane. Composites Commun Elsevier. 2020;21:100382.
- Li H, Liang Y, Li P, He C. Conversion of biomass lignin to highvalue polyurethane: a review. J Bioresource Bioprod Elsevier. 2020;5:163–79.
- Bergamasco S, Tamantini S, Zikeli F, Vinciguerra V, Scarascia-Mugnozza G, Romagnoli M. Synthesis and characterizations of eco-friendly organosolv lignin-based polyurethane coating films for the coating industry. Polymers MDPI. 2022;14:416.
- Kumar S, Mukherjee A, Dutta J. Chitosan based nanocomposite films and coatings: emerging antimicrobial food packaging alternatives. Trends Food Sci Technol. 2020;97:196–209.
- Zhao W, Yu D, Xia W. Vacuum impregnation of chitosan coating combined with water-soluble polyphenol extracts on sensory, physical state, microbiota composition and quality of refrigerated grass carp slices. Int J Biol Macromol. 2021;193:847–55.
- Sanchez-Salvador JL, Balea A, Monte MC, Negro C, Blanco A. Chitosan grafted/cross-linked with biodegradable polymers: a review. Int J Biol Macromol. 2021;178:325–43.
- 31. Esfandiar N, Elmi F, Omidzahir S. Study of the structural properties and degradation of coated wood with polydopamine/ hydroxyapatite/chitosan hybrid nanocomposite in seawater. Cellulose. 2020;27:7779–90.
- Silva-Castro I, Casados-Sanz M, Alonso-Cortés A, Martín-Ramos P, Martín-Gil J, Acuña-Rello L. Chitosan-based coatings to prevent the decay of Populus spp. wood caused by Trametes versicolor. Coatings. 2018;8:415.
- Andok A, Jesuet MSG. Biodegradable chitosan coating for wood protection. IOP Conf Ser : Earth Environ Sci. 2022;1053:012036.
- 34. Manickavasagan A, Lim L-T, Ali A. Plant protein foods. Springer Cham; 2022.
- Feng B, Wang D, Li Y, Qian J, Yu C, Wang M, et al. Mechanical properties of a soy protein isolate–grafted–acrylate (SGA) copolymer used for wood coatings Polymers. Multidisc Dig Publish Instit. 2020;12:1137.
- Leong WI, Lo OLI, Cheng FT, Cheong WM, Seak LCU. Using recombinant adhesive proteins as durable and green flameretardant coatings. Synth Syst Biotechnol. 2021;6:369–76.
- Vothi H, Nguyen C, Pham LH, Hoang D, Kim J. Novel nitrogen–phosphorus flame retardant based on phosphonamidate: Thermal stability and flame retardancy. ACS Omega ACS Publ. 2019;4:17791–7.
- Uddin M, Kiviranta K, Suvanto S, Alvila L, Leskinen J, Lappalainen R, et al. Casein-magnesium composite as an intumescent fire retardant coating for wood. Fire Saf J. 2020;112:102943.
- Allasia M, Aguirre M, Gugliotta LM, Minari RJ, Leiza JR. High biobased content waterborne latexes stabilized with casein. Prog Org Coat. 2022;168:106870.
- 40. Raychura AJ, Jauhari S, Dholakiya BZ. Development of wood protective polyurethane coatings from mahua oil-based polyetheramide polyol: a renewable approach. Soft Mater Taylor Francis. 2018;16:209–19.
- 41. Raychura AJ, Jauhari S, Patel KI, Dholakiya BZ. A renewable approach toward the development of mahua oil-based wood

protective polyurethane coatings: synthesis and performance evaluation. J Appl Polymer Sci. 2018;135:46722 Wiley Online Library.

- 42. Llorente O, Barquero A, Paulis M, Leiza JR. Challenges to incorporate high contents of bio-based isobornyl methacrylate (IBOMA) into waterborne coatings. Prog Org Coat. 2022;172:107137.
- 43. Paraskar PM, Prabhudesai MS, Hatkar VM, Kulkarni RD. Vegetable oil based polyurethane coatings–a sustainable approach: a review. Progress Organic Coatings. 2021;156:106267.
- Trache D, Tarchoun AF, Derradji M, Hamidon TS, Masruchin N, Brosse N, et al. Nanocellulose: from fundamentals to advanced applications. Front Chem Front Media SA. 2020;8:392.
- 45.•• Cherian RM, Tharayil A, Varghese RT, Antony T, Kargarzadeh H, Chirayil CJ, et al. A review on the emerging applications of nano- cellulose as advanced coatings. Carbohydr Polym. 2022; 282, 119123. This paper relates the importance of nanocellulose as an additive in coatings and its use in the following fields: biomedical, green electronics, food packaging and as an anti-fouling. The paper discusses these aspects of nanocellulose-based coatings as well as their challenges and prospects
- 46. Pacheco CM, Cecilia BA, Reyes G, Oviedo C, Fernández-Pérez A, Elso M, et al. Nanocomposite additive of SiO2/TiO2/nanocellulose on waterborne coating formulations for mechanical and aesthetic properties stability on wood. Mater Today Commu. 2021;29:102990.
- Hochmańska-Kaniewska P, Janiszewska D, Oleszek T. Enhancement of the properties of acrylic wood coatings with the use of biopolymers. Progress Organic Coatings. 2022;162:106522.
- Kong L, Xu D, He Z, Wang F, Gui S, Fan J, et al. Nanocellulosereinforced polyurethane for waterborne wood coating. Molecules MDPI. 2019;24:3151.
- Norrrahim MNF, Nurazzi NM, Jenol MA, Farid MAA, Janudin N, Ujang FA, et al. Emerging development of nanocellulose as an antimicrobial material: an overview. Mater Adv Royal Soc Chem. 2021;2:3538–51.
- Thompson L, Azadmanjiri J, Nikzad M, Sbarski I, Wang J, Yu A. Cellulose nanocrystals: production, functionalization and advanced applications. Rev Adv Mater Sci De Gruyter Open Access. 2019;58:1–16.
- Kluge M, Veigel S, Pinkl S, Henniges U, Zollfrank C, Rössler A, et al. Nanocellulosic fillers for waterborne wood coatings: reinforcement effect on free-standing coating films. Wood Sci Technol Springer. 2017;51:601–13.
- 52. Soidinsalo, Holtan, Moosavifar. Microfibrillated cellulose: a novel and renewable multifunctional additive for waterborne coatings [Internet]. Coatings World. 2019. Available from: https://www.coatingsworld.com/issues/2019-06-01/view\_ technical-papers/microfibrillated-cellulose-a-novel-and-renew able-multifunctional-additive-for-waterborne-coatings#:~:text= Microfibrillated%20cellulose%20(MFC)%20is%20a,rheology% 2C%20stabilization%20and%20surface%20properties. Accessed 2 Aug 2023.
- Rajinipriya M, Nagalakshmaiah M, Robert M, Elkoun S. Importance of agricultural and industrial waste in the field of nanocellulose and recent industrial developments of wood based nanocellulose: a review. ACS Sustain Chem Eng ACS Publ. 2018;6:2807–28.
- Kobeticova K, Böhm M, Ďurišová K, Nabelkova J, Černý R. Chitin-caffeine models in biocidal wood coatings. In: International Conference of Chemical Technology 2021 – Book of Proceedings; 2022.
- 55. Li S, Wang X, Xu M, Liu L, Wang W, Gao S, et al. Effect of a biomass based waterborne fire retardant coating on the flame retardancy for wood. Polymers Adv Technol. 2021;32:4805–14 Wiley Online Library.

- El Knidri H, Belaabed R, Addaou A, Laajeb A, Lahsini A. Extraction, chemical modification and characterization of chitin and chitosan. Int J Biol Macromole Elsevier. 2018;120:1181–9.
- Mikame K, Ohashi Y, Naito Y, Nishimura H, Katahira M, Sugawara S, et al. Natural organic ultraviolet absorbers from lignin. ACS Sustain Chem Eng ACS Publ. 2021;9:16651–8.
- Zhang Y, Naebe M. Lignin: a review on structure, properties, and applications as a light-colored UV absorber. ACS Sustain Chem Eng ACS Publ. 2021;9:1427–42.
- 59. Sadeghifar H, Ragauskas A. Lignin as a UV light blocker—a review. Polymers MDPI. 2020;12:1134.
- Bahmani M, Schmidt O. Plant essential oils for environmentfriendly protection of wood objects against fungi. Maderas Ciencia y Tecnología SciELO Chile. 2018;20:325–32.
- Šimůnková K, Hýsek Š, Reinprecht L, Šobotník J, Lišková T, Pánek M. Lavender oil as eco-friendly alternative to protect wood against termites without negative effect on wood properties. Sci Rep Nat Publish Group. 2022;12:1–10.
- 62. Kwaśniewska-Sip P, Cofta G, Nowak PB. Resistance of fungal growth on Scots pine treated with caffeine. Int Biodeterior Biodegrad Elsevier. 2018;132:178–84.
- 63. Oberle A, Paschová Z, Bak M, Gryc V. Beech wood impregnation with hydrolyzed wattle tannin. Bioresources. 2021;16:2548–56.
- 64. Tomak ED, Ustaomer D, Yildiz S, Pesman E. Changes in surface and mechanical properties of heat treated wood during natural weathering. Measurement. 2014;53:30–9.
- Ermeydan MA. A natural flavonoid, chrysin, improving wood properties via impregnation. BioResources. 2019;14:2133–43.
- Woźniak M, Kwaśniewska-Sip P, Waśkiewicz A, Cofta G, Ratajczak I. The possibility of propolis extract application in wood protection. Forests MDPI. 2020;11:465.
- 67.•• Teacă C-A, Roşu D, Mustață F, Rusu T, Roşu L, Roşca I, et al. Natural bio-based products for wood coating and protection against degradation: a review. BioRes. 2019;14:4873–901. This article explains the use of biobased coatings to protect wood substrates. It introduces the natural products that can be used to protect wood, such as extractives from wood and plants with biocides properties, plant oils, waxes, resins, and biopolymers
- Hodges TW, Kemp LK, Mcinnis BM, Wilhelm KL, Hurt JD, Mcdaniel S, et al. Proteins and peptides as replacements for traditional organic preservatives: Part I [Internet]. 2022. Available from: https://www.paint.org/coatingstech-magazine/articles/ proteins-and-peptides-as-replacements-for-traditional-organicpreservatives-part-i/. Accessed 2 Aug 2023.
- McDaniel S, McInnis BM, Hurt JD, Kemp LK, Hodges TW. Biotechnology meets coatings preservation. Coat. World. 2019;12:33–42.
- Farjana SH, Huda N, Mahmud MP. Life-cycle environmental impact assessment of mineral industries. IOP Conf Ser : Mater Sci Eng. 2018;351:012016.
- 71. BioPowder [Internet]. 2021. Available from: https://www.biopowder.com/en/. Accessed 7 Oct 2022.
- Tusso-Pinzón RA, Castillo-Landero A, Matallana-Pérez LG, Jiménez-Gutiérrez A. Intensified synthesis for ethyl lactate production including economic, sustainability and inherent safety criteria. Chem Eng Process-Process Intensif. 2020;154:108041.
- Román-Ramírez LA, Powders M, McKeown P, Jones MD, Wood J. Ethyl lactate production from the catalytic depolymerisation of post-consumer poly (lactic acid). J Polymers Environ. 2020;28:2956–64.
- Nanda B, Sailaja M, Mohapatra P, Pradhan RK, Nanda BB. Green solvents: a suitable alternative for sustainable chemistry. Mater Today: Proceed Elsevier. 2021;47:1234–40.
- 75. Guzman Barrera NI. Eco-compatible syntheses of bio-based solvents for the paint and coating industry [Thesis, Internet].

Institut National Polytechnique de Toulouse. 2018. Available from: https://oatao.univ-toulouse.fr/25250/. Accessed 2 Aug 2023.

- White SR, Sottos NR, Geubelle PH, Moore JS, Kessler MR, Sriram SR, et al. Autonomic healing of polymer composites. Nat Nat Publish Group. 2001;409:794–7.
- Yan X, Tao Y, Chang Y. Effect of shellac waterborne coating microcapsules on the optical, mechanical and self-healing properties of waterborne primer on Tilia europaea L. wood. Coatings MDPI. 2021;11:785.
- Peng W, Yan X. Preparation of tung oil microcapsule and its effect on wood surface coating. Polymers MDPI. 2022;14:1536.
- Chen X, Dam MA, Ono K, Mal A, Shen H, Nutt SR, et al. A thermally re-mendable cross-linked polymeric material. Sci Am Assoc Adv Sci. 2002;95:1698–702.
- Canadell J, Goossens H, Klumperman B. Self-healing materials based on disulfide links. Macromole ACS Publ. 2011;44:2536–41.
- Cordier P, Tournilhac F, Soulié-Ziakovic C, Leibler L. Self-healing and thermoreversible rubber from supramolecular assembly. Nat Nat Publish Group. 2008;451:977–80.
- Paquet C, Schmitt T, Klemberg-Sapieha JE, Morin J-F, Landry V. Self-healing UV curable acrylate coatings for wood finishing system, part 1: impact of the formulation on self-healing efficiency. Coatings MDPI. 2020;10:770.
- Sun F-C, Fu J-H, Peng Y-X, Jiao X-M, Liu H, Du F-P, et al. Dualfunctional intumescent fire-retardant/self-healing water-based plywood coatings. Progress Organic Coat. 2021;154:106187.
- Zhang L, Huang Y, Sun P, Hai Y, Jiang S. A self-healing, recyclable, and degradable fire-retardant gelatin-based biogel coating for green buildings. Soft Matter Royal Soc Chem. 2021;17:5231–9.
- Ou R, Eberts K, Skandan G, Lee SP, Iezzi R, Eberly DE. Selfhealing polymer nanocomposite coatings for use on surfaces made of wood. US Patent 8664298B1. 2014.
- Cho W, Shields JR, Dubrulle L, Wakeman K, Bhattarai A, Zammarano M, et al. Ion–complexed chitosan formulations as effective fire-retardant coatings for wood substrates. Polymer Degra Stab. 2022;197:109870.
- Traoré B, Brancheriau L, Perré P, Stevanovic T, Diouf P. Acoustic quality of vène wood (Pterocarpus erinaceus Poir) for xylophone instrument manufacture in Mali. Ann For Sci. 2010;67:815–815.
- Zhou L, Fu Y. Flame-retardant wood composites based on immobilizing with chitosan/sodium phytate/nano-TiO2-ZnO coatings via layer-by-layer self-assembly. Coat Multidisc Dig Publish Instit. 2020;10:296.
- Yan Y, Dong S, Jiang H, Hou B, Wang Z, Jin C. Efficient and durable flame-retardant coatings on wood fabricated by chitosan, graphene oxide, and ammonium polyphosphate ternary complexes via a layer-by-layer self-assembly approach. ACS Omega ACS Publ. 2022;7:29369–79.
- Ma X, Chen J, Zhu J, Yan N. Lignin-based polyurethane: recent advances and future perspectives. Macromole Rapid Commu. 2021;42:2000492 Wiley Online Library.
- Wang T, Li L, Cao Y, Wang Q, Guo C. Preparation and flame retardancy of castor oil based UV-cured flame retardant coating containing P/Si/S on wood surface. Industrial Crops Prod Elsevier. 2019;130:562–70.
- Jaramillo AF, Díaz-Gómez A, Ramirez J, Berrio ME, Cornejo V, Rojas D, et al. Eco-friendly fire-resistant coatings containing dihydrogen ammonium phosphate microcapsules and tannins. Coatings MDPI. 2021;11:280.
- 93. Solis-Pomar F, Díaz-Gómez A, Berrío ME, Ramírez J, Jaramillo AF, Fernández K, et al. A dual active-passive coating with intumescent and fire-retardant properties based on high molecular

weight tannins. Coatings MDPI. 2021;11:460. This paper demonstrated that tannins obtained from the waste of Pinus radiata bark are beneficial additives in the formulation of fire-resistant coatings. The combination of intumescent-fire retardant layers in a coating scheme showed better fire resistance results and improved mechanical properties compared to commercial products.

- Price EJ, Covello J, Paul R, Wnek GE. Tannic acid based superintumescent coatings for prolonged fire protection of cardboard and wood. SPE Polymers Wiley Online Library. 2021;2:153–68.
- 95. Huang Y, Ma T, Wang Q, Guo C. Synthesis of biobased flame-retardant carboxylic acid curing agent and application in wood surface coating. ACS Sustain Chem Eng ACS Publ. 2019;7:14727–38.
- Ghasemlou M, Daver F, Ivanova EP, Adhikari B. Bio-inspired sustainable and durable superhydrophobic materials: from nature to market. J Mater Chem A Royal Soc Chem. 2019;7:16643–70.
- 97. Yue D, Lin S, Cao M, Lin W, Zhang X. Fabrication of transparent and durable superhydrophobic polysiloxane/SiO2 coating on the wood surface. Cellulose. 2021;28:3745–58.
- Wang Q, Sun G, Tong Q, Yang W, Hao W. Fluorine-free superhydrophobic coatings from polydimethylsiloxane for sustainable chemical engineering: preparation methods and applications. Chem Eng J. 2021;426:130829.
- Yang H, Wang J, Zhao P, Mu H, Qi D. UV-assisted multiscale superhydrophobic wood resisting surface contamination and failure. ACS Omega Am Chem Soc. 2021;6:26732–40.
- Cui M, Qing Y, Yang Y, Long C, Liu C. Nanofunctionalized composite-crosslinked epoxy resin for eco-friendly and robust superhydrophobic coating against contaminants. Colloids Surf, A. 2022;633:127914.
- Olson E, Blisko J, Du C, Liu Y, Li Y, Thurber H, et al. Biobased superhydrophobic coating enabled by nanoparticle assembly. Nanoscale Adv Royal Soc Chem. 2021;3:4037–47.
- Yang J, Li H, Yi Z, Liao M, Qin Z. Stable superhydrophobic wood surface constracting by KH580 and nano-Al2O3 on polydopamine coating with two process methods. Colloids Surf, A. 2022;637:128219.
- 103. Shang Q, Chen J, Liu C, Hu Y, Hu L, Yang X, et al. Facile fabrication of environmentally friendly bio-based superhydrophobic surfaces via UV-polymerization for self-cleaning and high efficient oil/water separation. Prog Org Coat. 2019;137:105346.
- Arminger B, Gindl-Altmutter W, Keckes J, Hansmann C. Facile preparation of superhydrophobic wood surfaces via spraying of aqueous alkyl ketene dimer dispersions. RSC adv Royal Soc Chem. 2019;9:24357–67.
- Arminger B, Gindl-Altmutter W, Hansmann C. Efficient recovery of superhydrophobic wax surfaces on solid wood. Eur J Wood Wood Prod. 2022;80:345–53.
- 106 Saji VS. Wax-based artificial superhydrophobic surfaces and coatings. Colloids Surface A Physicochem Eng Aspects. 2020;602:125132.
- Janesch J, Arminger B, Gindl-Altmutter W, Hansmann C. Superhydrophobic coatings on wood made of plant oil and natural wax. Prog Org Coat. 2020;148:105891.