Chapter

Biopolymers as Coating Additives for Engineered Wood Products

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Abstract

Engineered wood products are used as a construction material due to enhance performance, faster and higher construction of buildings, durability, and less impact on the environment. However, its flammability and resistance to mold, insects and water limits its use in construction, and especially in exterior use. Thus, the necessity of developing wood coating formulations that reduce the impact of the environment and increases the durability of engineered wood products. Biopolymers have attracted considerable interest as alternatives in coating applications for engineered wood products due to their availability, environmentally friendly and compatibility with the main wood components. The focus of this book chapter is to give an overview of the treatment methods and bio-based coating of the engineered wood, with special emphasis on lignin-based coating. Lignin/lignin nanoparticles, due to the presence of functional groups, is a promising polymer for coating formulations and applications. Lignin can produce a significant quantity of char when heated at high temperatures. This is important combustion characteristic when lignin is to be used as coating additive for wood. As such, lignin-based fire retardant and antibacterial action of lignin are important properties when lignin-based coating formulations are developed, and they are discussed in this chapter.

Keywords: biopolymers, engineered wood products, lignin-based coating, lignin-fire retardant, antibacterial activity of lignin

1. Introduction

Engineered wood products are building materials that are made by laminating layers of wood together or by binding wood fibers together into a composite material, typically with an adhesive usually involving heat and/or pressure [1]. Engineered wood products offer consistency of structural performance and dimensional stability, making it possible to integrate them successfully with other construction materials on large and complex projects [2]. Engineered wood products are making it conceivable to build taller and bigger wood structures, which is highly asked by the building market [3]. There are many different types of engineered wood products, which can be categorized according to the type of feedstock used in their manufacture. The engineered wood association offer guidance on the properties and applications of engineered wood products being classified in three primary categories, as shown in **Figure 1**. Advantages of using engineered wood products compared to alternative

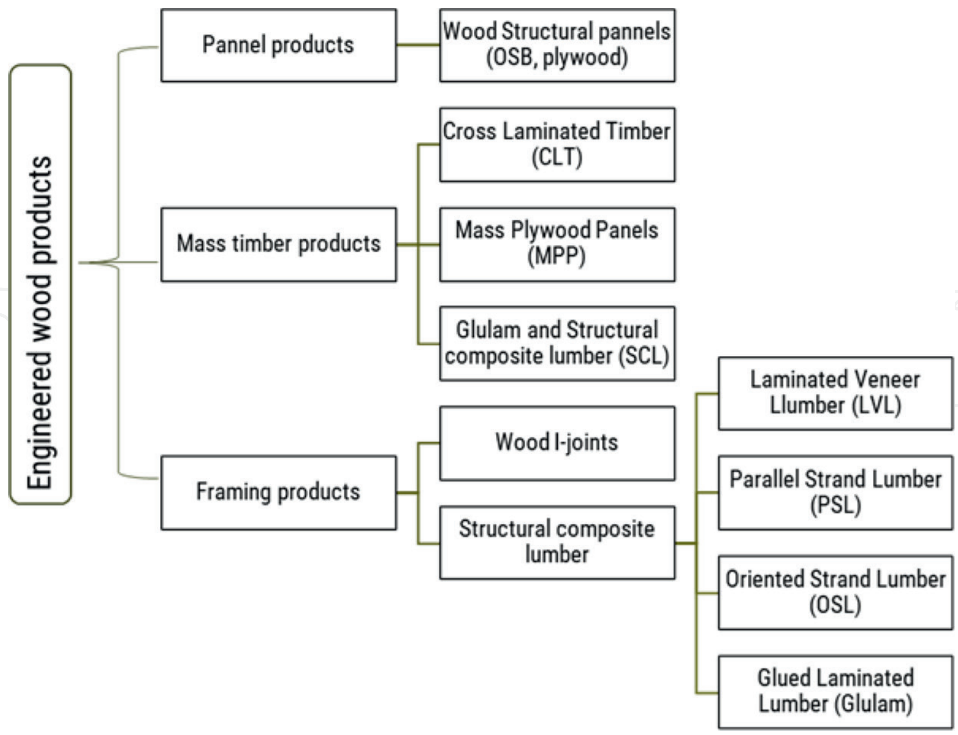

Figure 1.
The classification of engineered wood products, according to APA.

building materials are: (i) natural, renewable, sustainable and reduced carbon footprint; (ii) lighter-weight and greater flexibility in design and construction; (iii) faster and quitter construction; (iv) cheaper construction, warmth and esthetically pleasing with health benefits. Engineered wood products are considered to be renewable construction materials due to their composition [2].

A major factor supporting growth in the use of engineered wood products in construction is the increased environmental and sustainability concern [3, 4], which is influencing construction techniques and the choice of building materials. As such, wood is a renewable and sustainable building material used for modern engineering solutions and functional and decorative applications [5]. Wood has better insulating properties and a positive carbon balance compared to other building materials. Wood has much smaller carbon footprint than other construction materials, and increased use may reduce CO2 emissions by 14% [6]. Moreover, the greenhouse gas emissions have been shown to be as the same level as of concrete and lower than steel [7]. If properly maintained, wood can storage carbon for long lifespan. The engineered wood products used in exterior applications are maintained in time due to the use of preservatives such as creosote, halogenated carbamates, benzothiazoles, pentachlorophenol, (alkyl) imidazoles, bis(tributyltin) oxide, or salt-based impregnates [8, 9]. In addition, fire retardancy is an important behavior if the engineered wood products that are used in construction applications. Currently, the halogenated products are used as fire retardant additives for wood applications [10–13].

Both the currently used preservatives and halogenated fire-retardant additives used today are considered toxic, both for humans and environment. Preservative leaching problem when wood is encountering water and recyclability of wood materials when preservatives are used have been discussed by several authors [14–16]. As such, these concerns contribute to the necessity of developing non-toxic bio-based alternatives. Issues of sustainability and carbon sequestration opens the possibility for new green technologies which can improve durability, stability, and performance of wood, especially in exterior applications [17]. The wood preservative industry is interested in finding low-cost, environmentally friendly methods for the treatment of the wood [18]. Engineered wood products (EWP) producers recognize the potential to greatly expand their market-share if more optimal and affordable wood protection options can be found [1].

Extending the service life of wood and wood-derived products by using environmentally friendly biopolymers represents an attractive approach for wood protection from the perspectives of human health and environmental protection [19, 20]. The modern coating market is dominated by acrylic, polyurethane, and polyester polymer resins produced from unsustainable fossil resources. These coating additives are still used on the market due to their properties and low price. In the recent years, sustainable solutions such as vegetable-oil based coatings such as tall linseed, coconut, soybean, and castor-oil have been introduced on the market [21, 22] These oils are often used in different coating combinations to improve their properties. Usually, most of the additives used in coating applications requires chemical modification [21–24].

An environmentally friendly solution for wood preservation could be the use of biopolymers [25]. Biopolymers, due to the compatibility with the main wood components are considered as interesting alternatives to be used in coating applications [20]. Biopolymers not only that can enhance the performance of adhesives derived from petroleum in different ways [26], but also they can be used to develop environmental friendly and sustainable bio-based alternatives. Biopolymers are categorized as a function of their monomer unit in polysaccharides (cellulose, hemicellulose, glucans, starch), proteins (gelatin, casein), derived polypeptides (collagen, peptides) and polyphenols (tannins, lignin) [25, 27]. Biopolymer-based coatings can be directly deposited onto the substrate surface or by chemical reactions between the biopolymer and the substrate. The chosen coating technique is decided by a specific application, thus depending on several factors, described by Song et al. [28]. Biopolymers, due to the superior compatibility with the main components of wood, have a positive effect on the penetrability of biopolymer into the wooden mass and can enhance the biopolymer biocidal activity. Many other benefits, such as wood recyclability have been pointed out in the work of Patachia and Croitoru [29]. As such, this book chapter is important as it gives an overview on the use of biopolymers in coatings formulations and how these formulations can protect the wood against fire, insects, mold and water. Using natural biopolymers to replace the conventional preservatives and fire-retardant additives in wood protection is highly recommended, as the engineered wood product will be completely renewable and recyclable.

2. Treatment methods of engineered wood products

The drivers of using biopolymers-based additives in wood coating applications consist of sustainable concerns, such as increasing the durability of engineered wood products without the use of toxic compounds. In general, as described in the introduction part, wood can be protected against fungi, molds or insects by impregnation using different natural substances [30, 31]. Impregnation has been mostly applied on the solid wood, where the wood structure was chemically modified so that water penetration in the wood structure was limited. Chemical structure and composition of the engineered wood products allows efficient chemical modifications both at surface and inside the wood structure [32, 33]. As such, there is possible to tailor and synthesis recyclable and renewable engineered wood products with specific properties [18]. The uses of engineered wood products for exterior applications, such as in house-holds buildings requires both a surface and chemical treatment. Exterior wood coatings represent the second largest segment accounting 25% of the global architectural wood coatings market [7]. Different coatings formulations are designed to protect the wood from weathering degradation and preservation in outdoor conditions [34]. The coating agents act at the wood surface as barriers against environmental factors action, such as attack of insects, moisture and fire) and to maintain the aesthetical appearance of the wood. Plant oil-type wood preservatives, such as wood and plants extractives, vegetable oils, natural waxes, different biopolymers and biological control agents are the most applied one [31].

Both, high and low molecular mass biopolymers protect the wood against moisture, oxygen and biological attack. However, the mechanism between low and high molecular mass biopolymers is different. Biopolymers with high molecular mass can be used for surface impregnation, forming viscous biopolymer solutions which can minimize the leaching of biocidal compounds from the treated wood [35]. As such, biopolymer coating formulations can protect the environment and prolonging the lifecycle of wood [35]. Natural biopolymers, with low molecular mass generate solutions (aqueous or organic solvent based) with low viscosity, are proposed to be used as impregnation agents by diffusion into the wood. As such, by creating a film inside wood lumen and closing the pores, allows protection of the treated engineered wood products against water and biological attack. These low-molecular biopolymer solutions could be introduced into wood either by immersing (superficial impregnation) or by high-pressure impregnation [36, 37]. As such, enzymatic polymerization of essential oils with lignin in wood and treatments with nanoparticles [18], represents a promising solution to the engineered wood treatment as illustrated in **Figure 2**.

Currently, biopolymers are used in wood impregnation as aqueous dispersion or emulsions. However, new techniques for using biopolymers in wood modifications are developed in the last years such as biopolymer hydrogels, nanoparticles or biopolymer insertion by using an organic solvent as carrier. The hydrogels or the nanoparticles

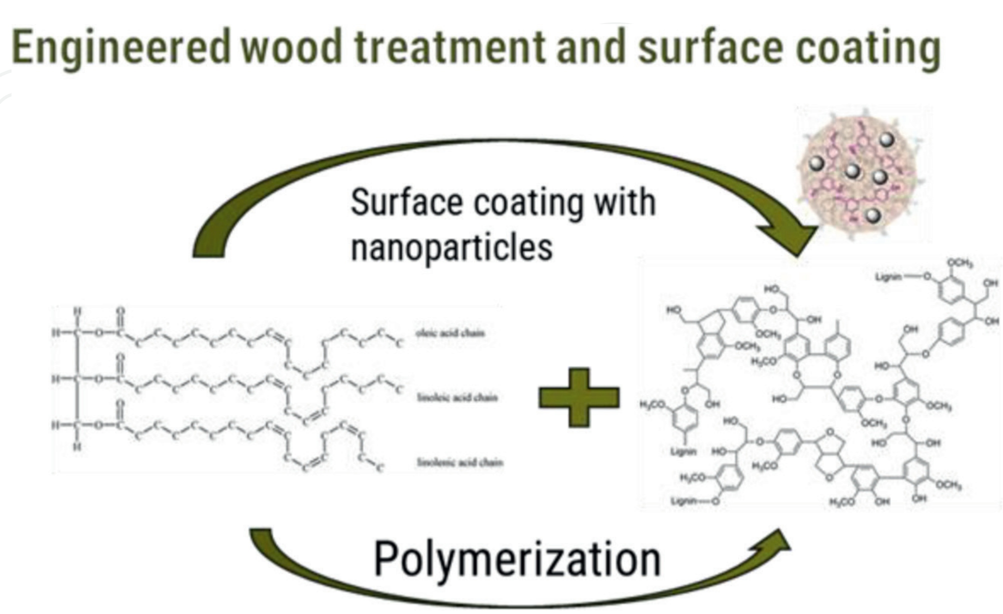

Figure 2.
Schematic figure of engineered wood treatment and surface coating.

can be loaded with biocides and within controlled conditions of temperature and moisture favors the swelling and the diffusion of hydrogels into the holes in the wood structure. As such, the biocide is fixed in the wood structure avoiding the leaching problem. When an organics solvent is used as carrier for the biopolymer, the same swollen mechanism was observed [38–40].

3. Bio-based coatings

In the last years, have bio-based adhesives gained considerable interest in the bonding of engineered wood products, as environmentally friendly approach compared to the conventional based adhesives. Natural biopolymers such as, cellulose, protein, lignin, and tannin and their modifications with different dispersing agents and cross-linkers have been successfully applied as adhesives for bonding of the engineered wood products [41]. Because of its hydrophobicity, lignin can be used as raw materials for coating [42]. Lignin, due to the presence of phenol groups in its structure, can successfully replace phenol in lignin-based adhesives formulations. Siahkamari et al. [43] developed a bio-based phenolic adhesive by entirely substituting both fossil-based phenol and formaldehyde with lignin and glyoxal.

3.1 Lignin-based coatings

Lignin, as a natural biopolymer from wood is produced as a by-product in many biorefinery processes. Currently, only about 1 million ton is used for value-added purposes, which mainly comprise in dispersants, adhesives, and fillers [44, 45]. Lignin has a complex chemical structure which includes hydroxyl, carboxyl and phenolic groups. The presence of these groups depends on the lignin isolation process. Chemical/enzymatic modification of lignin is often a necessity to introduce new functional groups that will increase compatibility between the components in the final material, illustrated in **Figure 3**. Interest in substituting fossil-based polymers with biopolymers in coating industry represents a great market opportunity in channeling recent developments into the production of green coating additives for engineered wood products. Lignin conversion to high quality products is critical to a biorefinery's profitability and sustainability. Organosolv lignin was esterified using dodecanoyl chloride to synthesize a hydrophobic coating for wood [46]. Literature studies show that lignin-based coatings have improved water repellent properties compared to conventional coatings formulations [46]. Henn et al. [47] demonstrated the preparation of fully particulate coatings without the use of binding matrix using lignin instead of metal oxides. Furthermore, colloidal lignin particles were exploited to prepare water-based, solvent free, and multiresistant surface coatings. Due to their hydroxyl groups, the colloidal lignin particles acted as hardener and required no binder to adhere to the substrate. As such, organosolv lignin has been successfully employed to prepare lignin-based epoxy resins [48].

Micro- and nanostructured coatings, such as colloidal lignin particles or lignin nanoparticles have gained attention because they disperse easy and due to their often excellent anticorrosion, antibacterial, anti-icing, and UV-shielding properties [49, 50]. It has been shown that high surface roughness of nanostructured coatings is one important factor contributing to their exceptional hydrophobicity [51, 52]. Hydrophobicity and abrasion of nanostructured coatings can be improved by binding or encapsulating the particles to a polymer/biopolymer matrix obtaining in this way a covalently particle-polymer matrix. As such, particle-polymer matrix can be applied

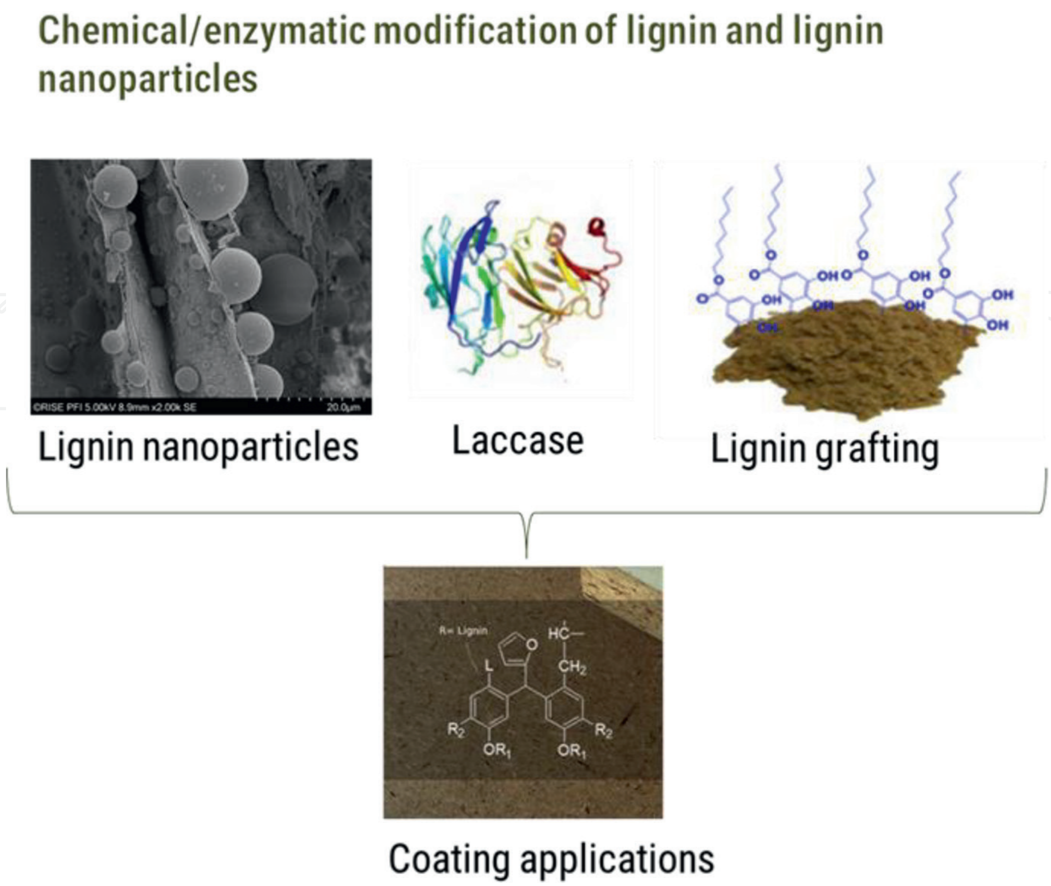

Figure 3.
Illustration of lignin nanoparticles, chemical/enzymatic modification of lignin.

for special applications being shown in the literature to give a very good water and abrasion protection, but at higher price [50, 53–55].

3.1.1 Lignin-based fire retardant

In recent research literature, it has been found that intumescent flame retardants, such as ammonium polyphosphate (APP), as a non-reactive, inorganic material can be added to polymers as a substitute for halogen flame retardant, being compatible with many polymers and biopolymers [56]. APP is a reaction results of ammonia and phosphoric acid. Therefore, as an additive used for intumescent coating in flame-retardant applications, APP has both function of acid and gas source. When a product containing APP meets fire, APP acts as a flame retardant by a chemical effect in the condensed phase called intumescence. As a result, a carbon foam is formed at the surface of the material which acts as an insulating layer, preventing further decomposition of the material. It has been shown that APP has high content of phosphorus and nitrogen, environmentally friendly, good thermal stability, low smoke, and nontoxicity [11]. These characteristics makes the intumescent flame superior to conventional flame retardants. In recent years, lignin and chitosan has been used as a carbon source in different flame-retardant formulations [12, 13, 57].

Lignin based flame retardants can be prepared by directly physical blending or by chemical modification [58, 59]. A disadvantage of the physical method is

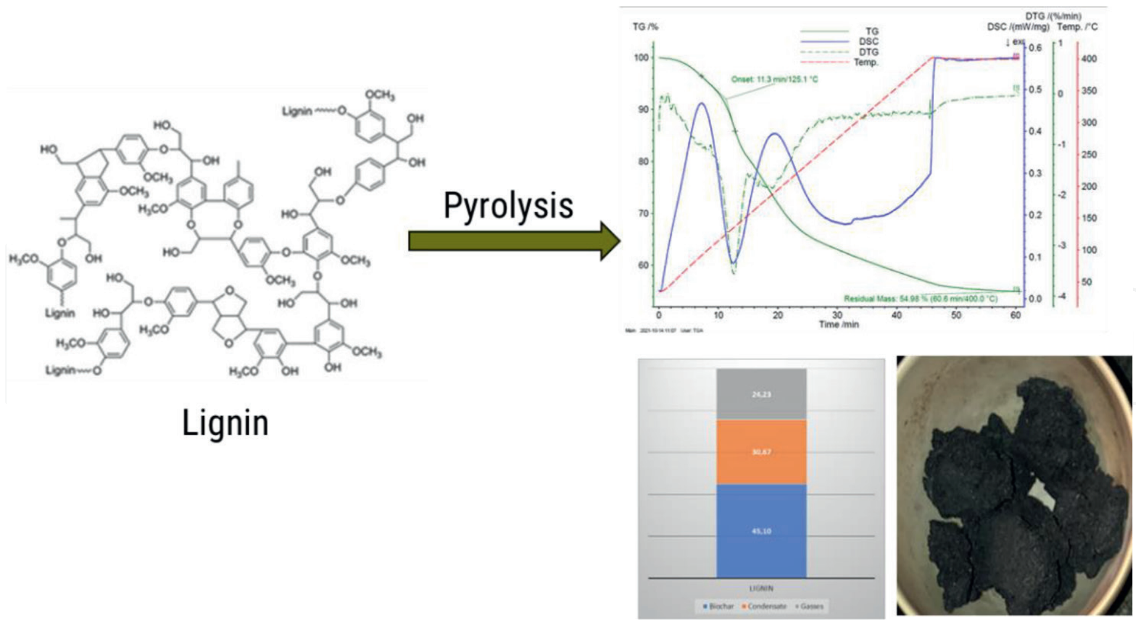

Figure 4.
Thermal decomposition of lignin.

uneven multicomponent mixing, which has a negative impact on flame retardancy. During the chemical modification, the hydroxyl groups present in lignin structure will react with desired functional groups, such as ammonia, phosphoric acid given a lignin with modified structure which is suitable to be used in intumescent flame-retardant formulations [60–63]. Zhang et al. [64] showed that lignin modified with urea and combined it with ammonium polyphosphate (APP) was successfully used as a novel intumescent flame retardant (IFR) system to improve the flame retardancy of polylactic acid (PLA). Moreover, Liu et al. [63] showed that novel lignin-based flame retardant was done by chemically grafting nitrogen, phosphorus and copper elements into lignin structure to improve the flame retardance of wood- plastic composites. Lignin nanoparticles can also be used in different intumescent flame-retardant formulations. Collet et al. used for the first-time lignin nanoparticles modified with phosphor in intumescent flame-retardant formulations [65].

Char yield during combustion of a polymer is an important characteristic when the polymer is to be used as a flame retardant or as additive for intumescent coating. We have observed that during thermal decomposition lignin produces high char yield up to 45%, as seen in **Figure 4**. We believe that the high char layer has a positive effect on smoke suppression and therefore er lignin a promising additive in intumescent flame-retardant formulations.

Our hypothesis on formation of a larger and denser charring layer helps in improving smoke suppression is in accordance with literature results of Dai et al. [59]. The mechanism involved here is similar when APP is used, where the hydroxyl groups present in lignin structure reacts with phosphoric acid and ammonia, as illustrated in **Figure 5.**

As such, both phosphor and nitrogen are introduced in lignin structure, having a function of an acid and gas source in intumescent flame-retardant formulations. We strongly believe that the synergic effect of both nitrogen and phosphor incorporated in lignin structure can improve the fire-resistance properties.

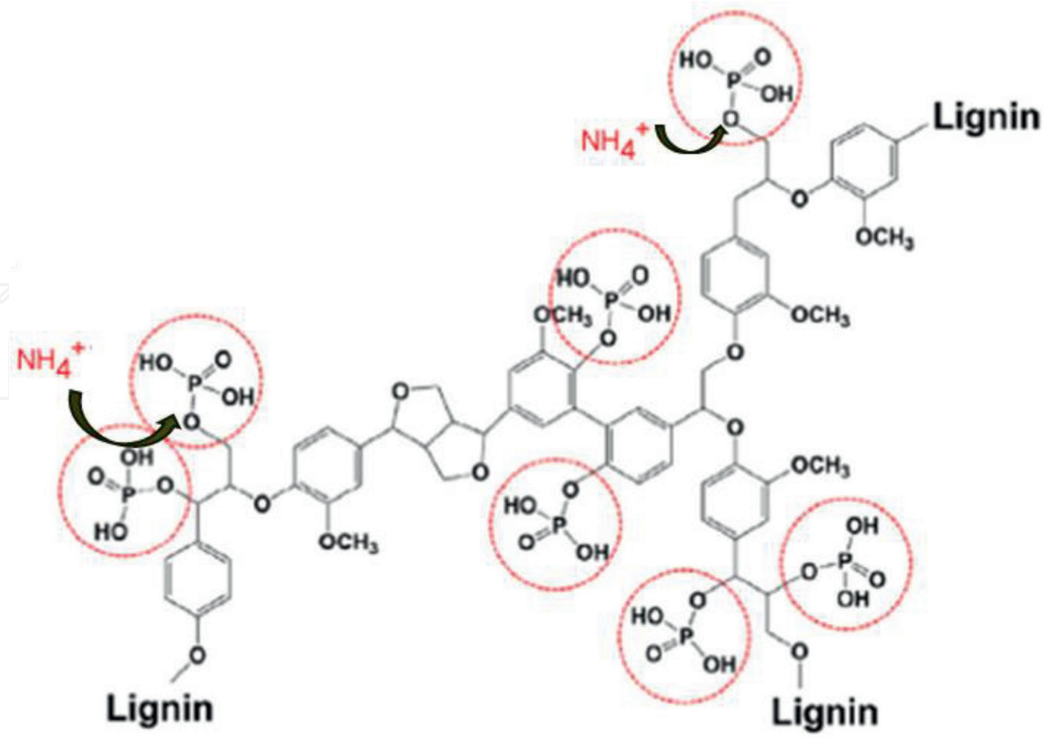

Figure 5.
Illustration of incorporation of phosphor and nitrogen in lignin structure.

3.1.2 Antibacterial activity of lignin

The antimicrobial property of biopolymers has been shown literature to depend on several factors, such as molecular mass, concentration, ability to be fixed into the wood structure and electrical charge [66]. Biopolymers with higher molecular masses have low biocidal activity, compared to high molecular mass biopolymers [67]. Literature studies shown that the antimicrobial activities of lignin can be inhibited by the presence phenolic monomers in lignin [68]. The lignin's antimicrobial activity depends on biomass source, the presence of hydroxyl and methoxy groups, and the extraction methods as follows: softwood organosolv > softwood kraft > grass organosolv due to the effect of acid-soluble lignin content [69]. Lignin as an antimicrobial agent is being used in commodity products like in plastic production [70], textile [71–73], medical materials, pest control, and healthcare products [74]. Lignin's and lignin nanoparticles chemical modification and combination with metals, for example Cu-lignin combination, have been shown to increase antimicrobial activity [75]. Thus, the use lignin as an antibacterial agent is believed to be a high value approach for lignin valorization.

4. Conclusions

Biopolymers are promising bio-based alternative to be used as biocides or barrier-forming compounds into the structure of wood. Designing a coating system with better performance on wood depends on understanding the interaction among individual wood constituents with the coating components. By using biopolymers as coating additives to protect the wood has environmental benefits and avoids the issue of wood recycling. Lignin based coating shows great potential in the future as a promising alternative to fossil-based polymers.

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Conflict of interest

The authors declare no conflict of interest.

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References

[1] William L. Improving the durability performance of engineered wood products: A study of Europe and North America, 2018 Gottstein fellowship report, Gold Coast. 2018

[2] Available from: https://cwc.ca/wp-content/uploads/2019/03/publications-casestudy Innovative ApplicationsEngineeredWood.pdf

[3] Yadav R, Kumar J. Engineered wood products as a sustainable construction material: A review. In: Engineered Wood Products for Construction. London, UK: IntechOpen Book; 2021. DOI: 10.5772/intechopen.99597

[4] Will the Skyscrapers of the Future be Made Out Of Wood? Available from: https://www.nationalgeographic.com/science/article/skyscrapers-of-the-future-will-be-made-out-of-wood

[5] Cunningham MF, Campbell JD, Fu Z, Bohling J, Leroux JG, Mabee W, Robert T. Future green chemistry and sustainability needs in polymeric coatings. Green Chemistry. 2019;21:4919-4926

[6] Oliver CD, Nassar NT, Lippke BR, McCarter JB. Carbon, fossil fuel and biodivesrsity mitigation with wood and forests 2014. Journal of Sustainable Forestry. 2014;**33**:248-275. DOI: 10.1080/10549811.2013.839386

[7] Wood coatings: only modest growth - News and insights for the European coatings industry (abtdgt.de)

[8] Betts WD. The properties and performance of coal-tar creosote as wood preservative. In: Thompson R, editor. The Chemistry of Wood Preservation. Amsterdam: Woodhead Publishing, Elsevier; 2005. pp. 117-135

[9] Bull DC. The chemistry of chromated copper arsenate II. Preservative wood-interactions. Wood Science and Technology. 2001;**34**:459-466

[10] Lu S, Hamerton I. Recent developments in the chemistry of halogen-free flame retardant polymers. Progress in Polymer Science. 2002;**27**:1661-1712

[11] Liang D, Zhu X, Dai P, Lu X, Guo H, Que H, et al. Preparation of a novel lignin-based flame retardant for epoxy resin. Materials Chemistry and Physics. 2021;**259**:124101. DOI: 10.1016/j.matchemphys.2020.124101

[12] Thakur VK, Thakur MK. Recent advances in graft copolymerization and applications of chitosan: A review. ACS Sustainable Chemistry & Engineering. 2014;**2**:2637-2652. DOI: 10.1021/sc500634p

[13] Yang HT, Yu B, Xu XD, Bourbigot S, Wang H, Song PA. Lignin-derived bio-based flame retardants toward high-performance sustainable polymeric materials. Green Chemistry. 2020;**22**:2129-2161. DOI: 10.1039/D0GC00449A

[14] Adam O, Badot PM, Degiorgi F, Crini G. Mixture toxicity assessment of wood preservative pesticides in the freshwater amphipod Gammarus pulex (L.). Ecotoxicology and Environmental Safety. 2009;**72**(2):441-449

[15] Lin LD, Chen YF, Wang SY, Tsai MJ. Leachability, metal corrosion, and termite resistance of wood treated with copper-based preservative. International Biodeterioration & Biodegradation. 2009;**63**(4):533-538

[16] Temiz A, Yildiz UC, Nilsson T. Effects of the wood preservatives on

mechanical properties of yellow pine (Pinus sylvestris L.) wood. Building and Environment. 2006;**41**(7):910-914

[17] Rowell MR editor. Chemical Modification of wood, Chapter 14. In: Handbook of Wood Chemistry and Wood Composites. Madison, WI: CRC Press LLC; 2005. pp. 381-420

[18] Teaca C-A, Rosu D, Mustata F, Rusu T, Rosu L, Rosca I, et al. Natural coatings for wood. BioReources. 2019;**14**(2):4873-4901

[19] Andok A, Jesuet MSG. Biodegradable chitosan coating for wood protection. IOP Conference Series: Environmental Earth Sciences. 1053, 012036

[20] Mazela B, Polus-Ratajczak I. Reduction of preservative leaching by animal proteins in wood. Holzforschung. 2003;**57**:593-596

[21] Lambourne R, Strivens T. Paint and surface coatings. Theory and Practice. 2000;**37**:1-18

[22] Alam M, Akram D, Sharmin E, Zafar F, Ahmad S. Vegetable oil based eco-friendly coating materials: A review article. Arabian Journal of Chemistry. 2014;**7**:469-479. DOI: 10.1016/j.arabjc.2013.12.023

[23] Gerardin P, Petric M, Petrissans M, Lambert J, J.J. Ehrhrardt evolution of wood surface free energy after heat treatment. Polymer Degradation and Stability. 2007;**92**:653-657

[24] Pizzi A. Wood products and green chemistry. Annals of Forest Science. 2016;**73**:185-206. DOI: 10.1007/s13595-014-0448-3

[25] Niaounakis M. Biopolymers Reuse, Recycling, and Disposal. Amsterdam, The Neherlands: Elsevier; 2013. pp. 1-75

[26] Heinrich LA. Future opportunities for bio-based adhesives - advantages beyond renewability. Green Chemistry. 2019;**21**:1866-1888

[27] Vroman I, Tighzert L. Biodegradable polymers. Materials. 2009;**2**:307-344

[28] Song X, Tang S, Chi X, Han G, Bai L, Shi QS, et al. Valorization of lignin from biorefinery: Colloidal lignin micro-Nanospheres as multifunctional bio-based fillers for waterborne wood coating enhancement. ACS Sustainable Chemistry & Engineering. 2022;**10**:11655-11665

[29] Patachia S, Croitoru C. Biopolymers for wood preservation. In: Biopolymers and Biotech Admixtures for Eco-Efficient Construction Materials. Elsevier Ltd.; 2016. pp. 305-332. DOI: 10.1016/B978-0-08-100214-8.00014-2

[30] Gonzalez-Laredo RF, Rosales-Castro M, Rocha-Guzman NE, Gallegos-Infante JA, Moreno-Jimenez MR, Karchesy JJ. Wood preservation using natural products. Madera y bosques. 2015;**21**:63-76. DOI: 10.21829/mub.2015.210427

[31] Rosu L, Varganici D-C, Mustata F, Rosu D, Rosca I, Rusu T. Epoxy coatings based on modified vegetable oils for wood surface protection against fungal degradation. ACS Applied Materials & Interfaces. 2020;**12**(12):14443-14458. DOI: 10.1021/acsami.0c00682

[32] Rowell MR. Understanding wood surface chemistry and approaches to wood modification: A review. Polymers. 2021;**13**:2558. DOI: 10.3390/polym13152558

[33] Farid T, Rafiq IM, Ali A, Tang W. Transforming wood as next-generation structural and functional materials for a sustainable future. EcoMat. 2022;**4**:12154. DOI: 10.1002/eom2.12154

[34] Nejad M, Cooper P. Exterior wood coatings. Chapter 6. In: Wood in Civil Engineering. InTechOpen; 2020. pp. 110-129. DOI: 10.5772/67170

[35] Singh AP, Singh T, Rickard C. Visualising impregnated chitosan in Pinus radiata early wood cells using light and scanning electron microscopy. Micron. 2010;**41**:263-267

[36] Freeman et al. Past, present, and future of the wood preservation industry. Forest Products Journal. 2003;**53**:8-15

[37] Singh T, Chittenden C, Singh AP, Franich R. Chitosan as a potential wood preservative. Wood Processing Newsletter. 2008;**42**:11-23

[38] Passialis C, Grigoriou A, Voulgaridis EV. Utilization of oleoresin and bark extractives from Pinus halepensis mill in wood products. Forêt méllilermnéenne. 1995;**16**(1):19-27

[39] Ding X, Richter D, Matuana L, Heiden P. Efficient one-pot synthesis and loading of self-assembled amphiphilic chitosan nanoparticles for low-leaching wood preservation. Carbohydrate Polymers. 2011;**86**(1):58-64

[40] Croitoru C, Patachia S, Lunguleasa A. A mild method of wood impregnation with biopolymers and resins using 1-ethyl-3-methylimidazolium chloride as carrier. Chemical Engineering Research and Design. 2015;**93**:257-268

[41] Islam NM, Rahman F, Das KA, Hixiroglu S. An overview of different types and potential of bio-based adhesives used for wood products. International Journal of Adhesion & Adhesives. 2022;**112**:102992

[42] Sreejaya MM, Jeeven SR, Ramanunni K, Pillai PN, Ramkumar K, Anuvinda P, et al. Lignin based organic coatings and their applications: A review. Materials Today: Proceedings. 2022;**60**:494-501

[43] Siahkamari M, Emmanuel S, Hodge BD, Nejad M. Lignin-glyoxal: A fully biobased formaldehyde-free wood adhesive for interior engineered wood products. ACS Sustainable Chemistry & Engineering. 2022;**10**:3430-3441. DOI: 10.1021/acssuschemeng.1c06843

[44] Ragauskas AJ et al. 2014 DOI: 10.1126/science.1246843,

[45] Grossman A, Vermerris W. 2019. DOI: 10.1016/j.copbio.2018.10.009

[46] Ferrari F, Striani R, Fico D, Mahbubul AM, Greco A, Corcione EC. An overview on wood waste valorizations of biopolymers and biocomposites: Definition, classification, production, properties and applications, review. Polymers. 2022;**14**(24):5519. DOI: 10.3390/polym14245519

[47] Henn AK, Forsman N, Zou T, Österberg M. Colloidal lignin particles and epoxies for bio-based, durable and multiresistant nanostructured coatings. ACS Applied Materials & Interfaces. 2021;**13**:34793-34806

[48] Over LC, Grau E, Grelier S, Meier MAR, Cramail H. Synthesis and characterization of epoxy thermosetting polymers from Glycidylated Organosolv lignin and bisphenol a. Macromolecular Chemistry and Physics. 2017;**218**(4):1600411

[49] Lintinen K, Xiao Y, Bangalore Ashok R, Leskinen T, Sakarinen E, Sipponen M, et al. Closed cycle production of concentrated and dry Redispersible colloidal lignin particles with a three solvent polarity

exchange method. Green Chemistry. 2018;**20**:843-850

[50] Bao W, Deng Z, Zhang S, Ji Z, Zhang H. Next-generation composite coating system: Nanocoating. Frontiers in Materials. 2019;**6**(72):1-6

[51] Forsman N, Lozhechnikova A, Khakalo A, Johansson LS, Vartiainen J, Österberg M. Layer-by-layer assembled hydrophobic coatings for cellulose Nanofibril films and textiles, made of Polylysine and natural wax particles. Carbohydrate Polymers. 2017;**173**:392-402

[52] Kosak Söz C, Yilgör E, Yilgör I. Influence of the average surface roughness on the formation of Superhydrophobic polymer surfaces through spin-coating with hydrophobic Fumed silica. Polymer. 2015;**62**:118-128

[53] Buss F, Roberts CC, Crawford KS, Peters K, Francis LF. Effect of soluble polymer binder on particle distribution in a drying particulate coating. Journal of Colloid and Interface Science. 2011;**359**:112-120

[54] De Francisco R, Tiemblo P, Hoyos M, González-Arellano C, García N, Berglund L, et al. Multipurpose ultra and Superhydrophobic surfaces based on Oligodimethylsiloxane-modified Nanosilica. ACS Applied Materials & Interfaces. 2014;**6**:18998-19010

[55] Das S, Kumar S, Samal SK, Mohanty S, Nayak SK. A review on Superhydrophobic polymer Nanocoatings: Recent development and applications. Industrial and Engineering Chemistry Research. 2018;**57**:2727-2745

[56] Bourbigot S, Le Bras M, Delobel R, Tremillon J-M. Synergistic effect of zeolite in an intumescence process. Study of the interactions between the polymer and the additives. Journal of the Chemical Society, Faraday Transactions. 1996;**92**:3435

[57] Gao C, Zhou L, Yao S, Qin C, Fatehi P. Phosphorylated Kraft lignin with improved thermal stability. International Journal of Biological Macromolecules. 2020;**162**:1642-1652

[58] Song P, Cao Z, Fu S, Fang Z, Wu Q, Ye J. Thermal degradation and flamr retardarncy properties of ABS/lignin: Effects of lignin content and reactive compatibilization. Thermochimica Acta. 2011;**518**:59-65

[59] Dai P, Liang M, Ma X, Luo Y, He M, Gu X, et al. Highly efficient, environmentally friendly lignin-based flame retardant used in epoxy resin. ACS Omega. 2020;**5**:32084-32093

[60] Liu L, Huang G, Song P, Yu Y, Fu S. Converting industrial alkali lignin to biobased functional additives for improving fire behavior and smoke suppression of polybutylene succinate. ACS Sustainable Chemistry & Engineering. 2016;**4**:4732-4742

[61] Costes L, Laoutid F, Aguedo M, Richel A, Brohez S, Delvosalle C, et al. Phosphorus and nitrogen derivatization as efficient route for improvement of lignin flame retardant action in PLA. European Polymer Journal. 2016;**84**:652-667

[62] Wu W, He H, Liu T, Wei R, Cao X, Sun Q, et al. Synergetic enhancement on flame retardancy by melamine phosphate modified lignin in rice husk ash filled P34HB biocomposites. Composites Science and Technology. 2018;**168**:246-254

[63] Liu L, Qian M, Song PA, Huang G, Yu Y, Fu S. Fabrication of green lignin-based flame retardants for enhancing the

thermal and fire retardancy properties of polypropylene/wood composites. ACS Sustainable Chemistry & Engineering. 2016;**4**:2422-2431

[64] Zhang R, Xiao X, Tai Q, Huang H, Hu Y. Modification of lignin and its application as char agent in itumecent flame retardant poly(lactic acid). Polymer Engineering and Science. 2012;**52**(12):2620-2626. DOI: 10.1002/pen.23214

[65] Collet B, Lopez-Cuesta J-M, Laoutid F, Fery L. Lignin nanoparticles as a promising way for enhancing lignin flame retardant effect in polylactide. Materials. 2019;**12**:2132. DOI: 10.3390/ma12132132

[66] Goy RC, de Britto D, Assis OBG. A review of the antimicrobial activity of chitosan. Polímeros. 2009;**19**(3):241-247

[67] Badawy MEI, Rabea EI. A biopolymer chitosan and its derivatives as promising antimicrobial agents against plant pathogens and their applications in crop protection. International Journal of Carbohydrate Chemistry. 2011;**3**:100-129

[68] Jung HG, Fahey GC. Nutritional implications of phenolic monomers and lignin: A review. Journal of Animal Science. 1983;**57**(1):206-219

[69] Alzagameem A, Klein ES, Bergs M, Tung DX, Korte I, Dohlen S, et al. Antimicrobial activity of lignin and lignin-derived cellulose and chitosan composites against selected pathogenic and spoilage microorganisms. Polymers. 2019;**11**:670. DOI: 10.3390/polym11040670

[70] Klein A, Rumpf K, Kreyenschmidt, and Schulze. Antimicrobial activity of LigninDerived polyurethane coatings prepared from unmodified and Demethylated Lignins. Coatings. 2019;**9**(8):494. DOI: 10.3390/coatings9080494

[71] Sriroth K, Sunthornvarabhas J. Lignin from sugar process as natural antimicrobial agent. Biochemistry and Pharmacology: Open Access. 2018;**07**(01):1-4. DOI: 10.4172/2167-0501.1000239

[72] Sunthornvarabhas J, Liengprayoon S, Suwonsichon T. Antimicrobial kinetic activities of lignin from sugarcane bagasse for textile product. Industrial Crops and Products. 2017;**109**:857-861. DOI: 10.1016/j.indcrop.2017.09.059

[73] Sunthornvarabhas J, Liengprayoon S, Lerksamran T, Buratcharin C, Suwonsichon TI, Vanichsriratana W, et al. Utilization of lignin extracts from sugarcane bagasse as bio-based antimicrobial fabrics. Sugar Tech. 2018;**21**(2):355-363. DOI: 10.1007/s12355-018-0683-2

[74] Gordobil O, Herrera R, Yahyaoui M, İlk S, Kaya M, Labidi J. Potential use of Kraft and Organosolv Lignins as a natural additive for healthcare products. RSC Advances. 2018;**8**(43):24525-24533. DOI: 10.1039/c8ra02255k

[75] Sinisi V, Pelagatti P, Carcelli M, Migliori A, Mantovani L, Righi L, et al. A green approach to copper-containing pesticides: Antimicrobial and antifungal activity of Brochantite supported on lignin for the development of biobased plant protection products. ACS Sustainable Chemistry & Engineering. 2018;**7**(3):3213-3221. DOI: 10.1021/acssuschemeng.8b05135