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Green Binders for Wood Adhesives

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Abstract

Today's society relies heavily on glued wood products for constructions, furniture, and floorings, for example. Essentially, all adhesives on the market are based on fossil-based resources, and many also contain formaldehyde to yield sufficient reactivity and adhesive performance. Formaldehyde is soon to be banned from consumer goods in Europe, due to its carcinogenic and allergenic features. With the rapidly growing societal environmental awareness, it becomes evident that it is crucial to seek greener, more sustainable alternatives. There is nothing new to this idea; on the contrary, prior to the advent of synthetic polymers, a range of biopolymers such as proteins and starch, were successfully used. However, since adhesives based on synthetic polymers were found to perform better, especially regarding the water resistance, the naturally sourced adhesives have had a subordinate role up until recently. The growing interest for using bio-polymers from renewable resources, such as wood/forest, corn, and cereals have spurred significant R&D developments toward the use of bio-polymers in green wood adhesives. The scope of the present chapter is to summarize, in short, some of the most recent scientific literature regarding the development of green adhesives.

Keywords: wood adhesive, protein, polysaccharide, starch, chitosan, hemicellulose, tannin, lignin

1. Introduction

Wood adhesives are produced in large amounts and are used for many large-scale applications such as load-bearing constructions, flooring, furniture, doors, and windows. Today, wood adhesives are essentially solely prepared from fossil-derived polymers based on, for example, urea, melamine, formaldehyde, phenol, resorcinol, isocyanate, and vinyl acetate, but historically adhesives were prepared from various natural sources, such as proteins

from milk, blood, and soybean [1]. In 1928, Casco Adhesives (now AkzoNobel Adhesives) in Sweden, started their production of adhesives based on casein (Casein Company), a milk protein [2]. With the rapid and revolutionizing development of the “plastic era,” initialized during the 1940s with the launch of synthetic polymers such as acrylates and vinyl esters, it became apparent that the performance of bio-based adhesives could be widely exceeded. During the 1960s, the hitherto used natural binders were replaced by synthetic polymers derived from fossil-based resources, motivated both by insufficient properties and high cost [3, 4].

Fossil-derived adhesives are cost-effective and perform very well regarding bonding performance and water resistance. The oil-crisis during the 1970s brought about a realization that natural sources for fossil-based products are limited; however, this has not yet had a dramatic effect on the adhesive industry. A large share of the industrially viable wood adhesive systems also comprises formaldehyde which is a highly reactive compound, making it well suited for its intended use. For instance, particleboard products are almost exclusively bonded with formaldehyde, in combination with urea and/or melamine or phenol. However, formaldehyde has been identified as a very hazardous compound and will most likely be banned from use in many applications [5]. The formaldehyde ban, combined with the rapidly growing environmental awareness calls for the adhesive industry to become more sustainable, more benign, and less fossil-dependent. To replace fossil-based adhesives with sustainable counterparts successfully, the adhesive properties and bonding performance have to be very similar, or bring other added values, and very importantly, the cost performance has to be on par with existing, non-sustainable, adhesives.

The urge for developing green adhesives reawakens the interest for bio-based adhesives, even though it is not completely uncomplicated. Many natural resources such as starch and protein, potentially well-suited for adhesive applications, may also be used as food sources. This calls for careful consideration in a time where more than 800 million people suffer from starvation world-wide [6].

The development of bio-based adhesives also poses other challenges; adhesives prepared from bio-based polymers often exhibit poor water resistance and/or render too high cost to successfully compete with fossil-derived polymers [1]. Another challenge when utilizing bio-based polymers is the often large property variation, emanating from locus and constantly shifting growth-conditions such as type of source, growth season, access to nutrients, climate, etc. [7]. Also, the extraction and fractionation procedures required to isolate the bio-based polymers will influence the final properties of the adhesive, as well as the cost. Altogether, it is challenging to replace robust synthetic polymers, having well-known and reproducible characteristics, with bio-based polymers with a broader property window, in industrial applications. Today, the research in this area is mainly focused on proteins, starch and other polysaccharides, lignin, and tannin as raw materials (**Figure 1**).

1.1. Evaluation of bonded specimens

Wood adhesives can be applied on several different substrates such as veneers, plywoods, panels, beams, particleboards, etc., and are often subjected to elevated temperatures and high

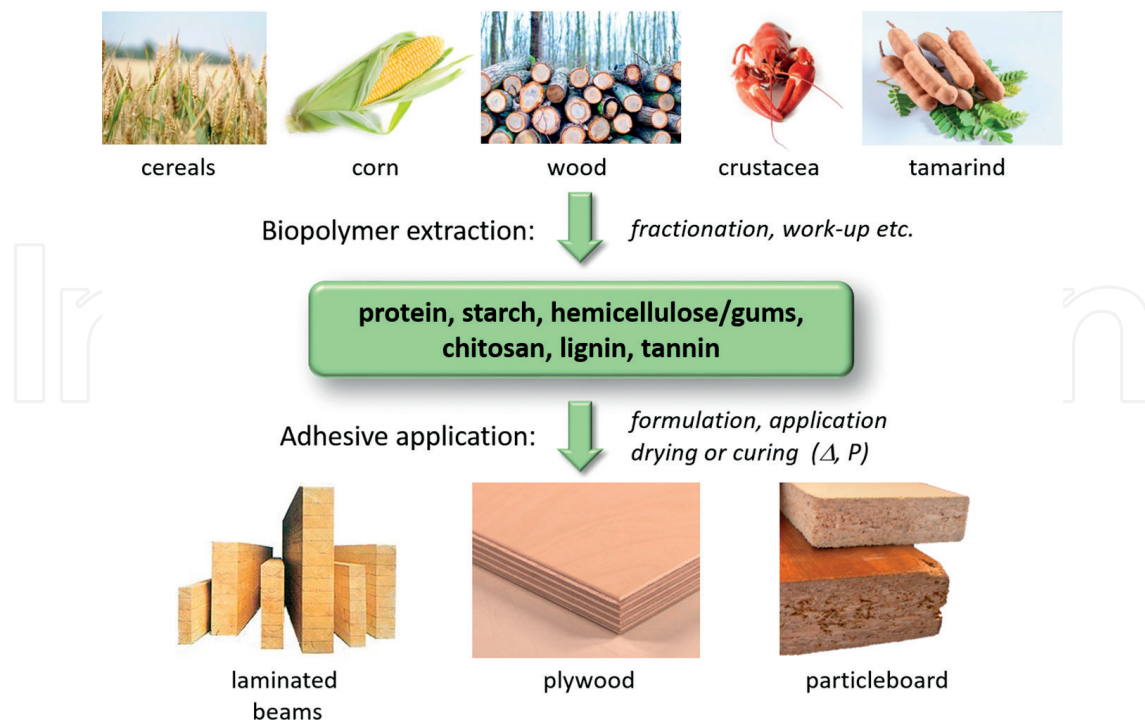


Figure 1. Green binders for wood adhesives. Photocredits for pictures of particleboard and plywood distributed by a CC-BY-SA 3.0 license [8].

pressure during cure depending on the application. Adhesives are evaluated by testing the bond strength of the bonded wood specimens; both dry and wet strength are crucial properties. The requirement of the adhesive depends on the application (e.g., interior or exterior use), type of adhesive (e.g., thermoplastic or thermosets), type of wood substrate, etc. Heat resistance is of particular interest for specimens glued with thermoplastic adhesives, since a thermoplastic material generally is more sensitive to heat than the thermosetting counterpart. There are many different national standardized evaluation procedures, such as ASTM, EN, Chinese industry standard, China National Standards, etc., with different criteria for fulfilling the requirements of a certain application. These standards often differ in the gluing procedure, sample preparation, pressing conditions, conditioning and performance evaluation. The use of slightly dissimilar standards and evaluation protocols make it difficult to compare different studies [9, 10]. The evaluation of mechanical properties of wood adhesives has been subject to substantial research [11].

The chemical composition of adhesives is often characterized with Fourier transform infrared spectroscopy (FTIR), nuclear magnetic resonance (NMR), and the relative average molecular weight is determined by size exclusion chromatography (SEC). Further characterization includes rheological studies (mainly the viscosity), thermal studies using differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA), contact angle measurements, and storage stability measurements. The bond line and the adhesive's penetration into the wood in the bonded specimens can be studied with optical microscopy (OM), scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), and energy dispersive X-ray spectroscopy (EDXS), etc.

The scope of this book chapter is to give a short overview of the most recent publications concerning the use of bio-polymers as promising sustainable resources for wood adhesives. Several extensive and in-depth reviews of the use of green wood adhesives are already published and these are referred to throughout the chapter, when appropriate. The chapter does not cover patents or scientific publications published in any other language than English.

2. Protein

Proteins are linear polyamides built up by amino acids, linked together with polypeptide bonds, and are, together with DNA, fat, and polysaccharides, the most important constituent in all living species. There are 20 different amino acids, either acidic, basic, or neutral depending on the structure of the side chain. The properties of a protein originates from its complex structure; the amino acid sequence (primary structure) is partly arranging into α -helices and β -sheets (secondary structure), side-chains interact to form a 3D-structure (tertiary structure), and the whole protein molecule interacts with other protein molecules to form a higher-order (quaternary) structure [12].

Proteins have a long history as binders in wood adhesives but were replaced by fossil-based polymers due to cost and insufficient properties, such as poor bond strength and water resistance [1]. The side-chains of the polypeptide chain contain functional groups that make the amino acid either hydrophilic or hydrophobic, and provide possibilities for interaction with hydroxyl or carboxyl groups in wood, and for crosslinking.

Generally, protein adhesives suffer from high viscosity, consequently demanding low solid content, and they commonly only meet the requirements for indoor applications due to poor water resistance [13]. Extensive research is being conducted to improve the bonding performance and water resistance of proteins to extend the applicability of wood-bonded protein adhesives, as previously reviewed in literature [13–15].

Soybean protein can be obtained from soybeans during the production of soy oil and soy meal. Soy oil is used in the food industry and soy meal as animal feed [16]. Soy protein is a promising alternative to fossil-based adhesives due to its availability, easy processing, and low cost, but the fact that it is a food source is debatable. Soybean protein-based adhesives have been suggested in a few applications today: particleboards, laminated plywood, and finger-joint lumber [13, 17]. So far, the use of soybean protein in adhesives has been limited due to low water resistance and high viscosity [13]. Adhesives containing soybean flour is commercially available [18].

Physical and chemical methods have been used to improve the properties of proteins. Denaturation of the native protein structure exposes functional groups buried within the 3D-structure of the protein, which may enable solubilization and bonding. The increased solubilization further makes it possible for the protein adhesive to flow better over the wood surface, forming hydrogen bonds with wood, and allows for subsequent chemical crosslinking. Denaturisation can be triggered by increased temperature, pressure, and changes in pH, as well as the addition of denaturants, such as urea guanidine hydrochloride, enzymes, SDS or other detergents [13, 19].

It was shown that a combination of thermal alkali degradation, thermal acid treatment, and crosslinking of soybean protein can provide an adhesive with better applicability regarding viscosity and bonding performance. Thermal alkali degradation lowers the viscosity and improves the technological applicability. Thermal acid treatment allows for the formation of an intermolecular network which improves the water resistance. Glyoxal, epoxy latex, polyisocyanate, and polyamide were evaluated as crosslinkers. The type of crosslinker, amount of crosslinker, and ratio of thermal alkali-degraded soybean protein to thermal acid-treated soybean protein, had important effects on the final adhesive properties. Polyamide is the preferred crosslinker due to its good crosslinking efficiency, miscibility with soybean protein, and low viscosity [20].

Thermo-chemical treatment of soybean protein in the presence of sodium sulfide or sodium dodecyl sulfate, followed by crosslinking with epichlorohydrin-modified polyamide (EMPA) showed promising results. The adhesive could withstand recurring hygrothermal treatment after which the wet strength fulfilled the required value for structural use [21].

Proteins have also been combined with synthetic polymers and resins such as formaldehyde, urea formaldehyde (UF), melamine urea formaldehyde (MUF), and dispersion polymers, such as polyvinyl acetate (PVAc) [14, 22]. The water resistance of protein adhesives can be improved by the addition of crosslinkers such as polyamidoamine-epichlorohydrin (PAE) resin or polymeric diphenylmethane diisocyanate (pMDI) [14].

In a recent study, water was substituted with egg white in a soybean-meal adhesive which was subsequently crosslinked with triglycidyl amine in an attempt to increase the solid content and to improve the water resistance of soybean protein-based adhesives. As a result, the solid content was increased, the viscosity was kept low, and the bonding performance was improved. The wet strength of the adhesive was superior to that of conventional UF resin and PAE-crosslinked soybean protein-based adhesive, and was comparable to that of melamine-modified UF resin [23].

A green route to prepare a soybean protein-based adhesive has been demonstrated by utilizing the polysaccharides and proteins in soy meal. First, the polysaccharides and proteins were separated, whereafter the polysaccharides were crosslinked with a green crosslinker, sodium hexametaphosphate, and subsequently blended with the proteins to form an interpenetrating network. After hot pressing, a stable glue line was formed that fulfills the requirements for plywood in interior use [24]. In another study, the polysaccharides were hydrolyzed and then crosslinked with the proteins through a Maillard reaction. The bonding performance, rheological properties, and thermal stability were improved and the adhesive also met the requirements for plywood in indoor applications [25].

Magnesium oxide (MgO) has been added to soybean protein-based adhesives to improve the bonding performance. In a recent study, MgO was used together with different fractions from soybean. It is preferable to use soy flour or soy meal directly without purification steps which would increase the cost of the final product. However, the purified soybean protein gave better adhesive properties together with MgO, compared with the polysaccharide-containing soy flour [26].

The water resistance of a soybean protein-based adhesive can be improved with the addition of 5,5-dimethyl hydantoin polyepoxide (DMHP). DMHP acts as a crosslinker during cure

while at the same time decreasing the wet-adhesive viscosity, improving the wetting and penetration of the adhesive, yielding a smooth surface and bonding performance. DMHP made it possible to increase the solid content, decrease the viscosity, and improve both dry and wet strength [27].

A new type of soybean protein-based adhesive has been presented where a soybean protein-acrylate emulsion-based adhesive was synthesized by mini-emulsion polymerization. Methyl methacrylate and butyl acrylate were polymerized using soybean protein as the protective colloid, resulting in an adhesive evaluated for plywood preparation. The bonding performance was, however, only slightly improved [28].

Soybean protein has been blended with ethylene glycol, diethylene glycol, and polyethylene glycols with different molecular weights. Ethylene glycol improved the wet strength of the adhesive which was suggested to be due to improved wettability and hydrogen bonding. Higher molecular weight polyols, however, decreased the wet strength of the adhesives [29].

Soybean protein has also been blended with lignin to improve the water resistance of the adhesive [30]. The lignin-particle size and the protein-to-lignin ratio significantly affected the bonding performance. Lignin with smaller particle size increased the wet strength of the adhesive [31]. Lignin amine was prepared by Fenton oxidation and subsequent reductive amination [32]. Addition of lignin amine to soybean protein-based adhesives has also shown to improve the bonding performance and water resistance.

Soybean protein and cottonseed protein isolates were mixed in different ratios and used as wood adhesives. Increasing fraction of soybean protein was deteriorating the adhesive properties. However, formulations with addition of ca 50% xylan, starch, or cellulose exhibited a retained hot-water resistance [33].

Soy crops are unfortunately not widespread over the world; therefore, the possibility of using other types of proteins has also been explored. Wheat gluten is a by-product from the production of wheat starch and bioethanol, and has been studied as a binder for wood adhesives with promising results [34–44]. Other proteins that have been evaluated are, for example, zein protein [45], pea protein [45], canola protein [46, 47], cotton-seed protein [47], triticale protein [48], and lupine protein [49, 50].

3. Polysaccharides

Polysaccharides, built up by hydroxyl-functional monosaccharides joined together by glycosidic bonds, are an interesting group of polymers that have shown potential as binders for wood adhesives [51]. A polysaccharide with high molar mass will provide cohesive strength to the adhesive; however, a high molar mass will also give higher viscosity. The formation of hydrogen bonds between hydroxyl groups in the polysaccharide and the substrate allows for strong adhesion to wood. However, the hydroxyl groups also render the polysaccharide hydrophilic, which has a negative impact on the water resistance of the final adhesive. Improving the water resistance of polysaccharides is a challenge that is subject to much research.

3.1. Starch

Starch is a polysaccharide that has shown great potential as a binder for wood adhesives [14, 15, 52]. Starch has attracted much attention because of its abundance, renewability, and low price. Starch consists of amylose and amylopectin. Amylose is a long, linear polymer of α -1,4-linked D-glucopyranose, and amylopectin is a branched polymer, much larger than amylose, with α -1,4-linked glucose segments connected with α -1,6-linked branch points. The proportion of amylose to amylopectin affects the properties of the wood adhesive.

Native starch is a very good binder for wood, but it suffers from insufficient water resistance, when modifications are necessary. Many strategies have been employed to improve the properties of starch-based wood adhesives. Starch is often combined with another component, for example, polyvinyl alcohol, or polyvinyl acetate, to increase water resistance [53, 54]. There are several studies on graft polymerizations from starch, commonly using vinyl acetate as monomer and ammonium persulfate as initiator [54–56]. Confocal Raman Microscopy has been used to study the homogeneity of vinyl acetate-grafted starch. It was shown that the graft efficiency was important and had a large effect on the bonding performance of the starch adhesive [57].

One of the main challenges with starch-based wood adhesives is the storage stability; lately, several studies have demonstrated how this can be improved. The effect of emulsifiers in wood adhesives with high starch content has been studied, since the addition of emulsifiers can allow for good dispersion and storage stability. A combination of lauryl sodium sulfate (LSS) and alkylphenol ethoxylates (APEO) can improve the flowability and stability of the adhesive. However, a substitute for APEO is necessary since APEO has a negative impact on the environment [58]. Heat treatment of starch prior to the grafting reaction has been shown to enhance the grafting efficiency and the storage stability [59]. Sucrose-fatty acid esters, derived from renewable sources, have been used as surfactants added prior to grafting a high amylose-containing starch with vinyl acetate. The addition of surfactant resulted in excellent storage stability and improved bonding performance. The thermal stability increased and it was suggested that aggregation of particles was impeded by the surfactant [60]. Addition of SDS has been shown to improve the dispersibility and storage stability of starch grafted with vinyl acetate [61]. Unfortunately, the bonding performance was decreased with the addition of SDS. By adding Na-montmorillonite, a nano-layered silicate, the bonding performance was improved. An addition of 5% Na-montmorillonite enhanced the strength both in dry and wet state; the viscosity slightly increased but the dispersibility and stability were retained [62].

Acid hydrolysis of starch is a common method that can be used to modify starch and improve the solubility and the viscosity of the adhesive. Acid hydrolysis results in breakage of hydrogen bonds between starch molecules, facilitating starch molecules to react with crosslinkers or grafting monomers. Excessive acid hydrolysis may, however, damage the structure. More recently, studies have been performed to better understand how acid hydrolysis can be used to improve bonding performance, water resistance, heat resistance, and storage stability of the adhesive [63, 64].

A starch wood adhesive has been synthesized by oxidation of starch and subsequent attachment of a silane coupling agent, followed by polymerization of butyl acrylate and vinyl acetate. The bonding performance and the thermal stability of the adhesive were improved [65]. Butyl acrylate-grafted starch also resulted in an adhesive with good stability. The bonding

performance was similar to a commercial polyvinyl acetate adhesive even after storage for 3 months [65]. In another paper, oxidized starch was grafted with acrylamide and butyl acrylate and thereafter crosslinked with vinyltriisopropoxysilane to yield an adhesive with improved bonding performance [66]. A γ -methacryloxypropyl trimethoxy silane coupling agent was also studied for crosslinking starch grafted with vinyl acetate. The resulting adhesive showed improved bond strength, storage stability, and shear-thinning properties [67].

An isocyanate pre-polymer has been used to crosslink starch to enhance the water resistance. The starch was prepared by oxidation, or esterification, to reduce the crystallinity and increase the reactivity, and thereafter crosslinked with isocyanate [68–70]. Carboxymethyl cellulose (CMC) is another component that has been added to a starch/isocyanate adhesive together with polyvinyl alcohol and borax to tailor the viscosity, solids content, bonding performance, and the interface compatibility between starch and isocyanate pre-polymer [71].

3.2. Chitosan

Chitosan is deacetylated chitin, which is a polysaccharide that exists in crustaceans such as shrimp and crab, and insects. Naturally, chitosan only occurs in *Mucoraceae* fungi, but chitosan is also readily available and abundant by means of easy and facile derivatization from chitin. It is estimated that 10 billion tons of chitin are synthesized every year by the related organisms [72]. Chitosan is a polysaccharide consisting of β -(1,4)-linked 2-acetamido-2-deoxy-D-glucopyranose (N-acetyl glucosamine) and 2-amino-2-deoxy-D-glucopyranose (glucosamine). Besides being an economically feasible bioresource, chitosan has received great attention for a wide range of commercial applications [73–76] as it is biodegradable, biocompatible, non-toxic, antimicrobial and has reactive amino side groups which allow for chemical modification.

Besides the molecular weight, the degree of deacetylation is particularly important for the adhesion properties of chitosan. Chitosan is characterized by reactive amino groups and numerous hydroxyl groups that can interact with many different functional groups and high molar mass that provides cohesive strength, which makes it an interesting group of materials. Chitosan is insoluble in most organic solvents but soluble in water at acidic pH due to protonation of the amino groups. Combined, these characteristics open up the possibility for new applications in the adhesive and binder area [77].

Chitosan has shown great potential as a binder in adhesives, with or without additives or crosslinkers, as reviewed in literature [77, 78]. Chitosan formulations were prepared by dissolving chitosan in acetic acid solution, often used to dissolve chitosan. Double-lap wood specimens were bonded and dried for 24 h at 40°C with no applied pressure. The adhesive showed good bond strength that could be further improved with the addition of glycerol and trisodium citrate dehydrate [79]. It has been reported that citric acid reacts with chitosan amine groups to form amide bonds [80] and glycerol acts as a plasticizer which takes part in the curing process [81]. However, all formulations were found to have poor water resistance. The penetration of rhodamine-labeled chitosan in a pinewood matrix was investigated using a micro-imaging technique. No in-depth penetration of high molecular weight chitosan was observed [79].

Chitosan has been modified with glucose via the Maillard reaction [82, 83], aiming at improving bonding properties. The effect of glucose addition to chitosans of varying molecular

weight was evaluated with respect to bonding properties [84]. It was found that the dry and wet strengths were improved for low-molecular-weight chitosan. However, addition of glucose had a negative impact on bonding properties of high-molecular-weight chitosan.

Chitosan adhesives have also been prepared in combination with konjak glucomannan (KGM) [85]. Compared with casein and soybean protein references, the chitosan-KGM adhesive showed better bonding performance, but was inferior to a UF resin [85]. The bonding performance of chitosan-KGM-polyvinyl alcohol adhesive was also modeled using the Box-Behnken design for response surface methodology [86]. Polypeptides have been used to react with aldehyde and amine groups present in KGM and chitosan, respectively. The wet strength was improved, but the dry strength deteriorated [87].

3.3. Hemicelluloses/gums

Hemicelluloses can be found together with cellulose and lignin in biomass such as wood, grass, and cereals, while gums can be found in seeds, plants, seaweeds or microorganisms for example. Hemicelluloses and gums are heteropolysaccharides consisting of sugars such as xylose, arabinose, mannose, glucose, galactose, and sugar acids, and their chemical composition and structure varies with species [51, 88]. Hemicelluloses have low molecular weight, the average degree of polymerization (DP) is typically 80–200, compared with gums or cellulose with DP of several thousands [7]. Hemicelluloses and gums are among the most abundant biopolymers in nature. By-products from forestry and agriculture are good sources of hemicelluloses. With the growing environmental awareness, the traditional pulp mill is converted into a biorefinery to make efficient use of all possible side streams. Apart from power and fuel production, the possibilities for deriving value-added chemicals are also exploited. The hemicellulose-rich hydrolysates, emanating from the pulping process, can be explored as a constituent for wood adhesives. However, the hemicelluloses in the dilute hydrolysate have rather low-molecular weight and the liquor also contains salts and other by-products; therefore, further fractionation/purification is needed before evaluated in wood adhesives. Hemicelluloses are similar to starch structurally, thus holding promise for adhesive applications; yet, the challenges regarding water resistance remain. Moreover, hemicelluloses, unlike starch, have the advantage of not being a food source.

Locust bean gum (LBG), guar, tamarind, and xanthan gum have been evaluated as wood adhesives [89]. LBG, a galactomannan, obtained from seeds from the carob tree, has shown promising properties. A water dispersion of LBG exhibited very good bond strength, water resistance, and heat resistance [89]. A bacterial polysaccharide, FucoPol, has been tested as a binder for wood. The bond strength was fairly good, but the water resistance was very poor [90]. Another bacterial polysaccharide, xanthan gum, has been evaluated in wood adhesives [89, 91]. Xanthan gum by itself does not show any water resistance, but oxidized xanthan gum, on the other hand, show water resistance similar to polyurethane and chitosan adhesives. No significant improvement was observed by combining xanthan gum with chitosan [91]. Gum Arabic has been evaluated to produce particleboards that noticeably improved the overall panel properties. The particleboard had a smooth surface, and improved internal bond strength [92]. It has been reported that KGM can be used as a wood adhesive with good bond strength and stability [93]; however, low water resistance is limiting its applicability in wood adhesives [85]. The adhesion of KGM on plywood has been investigated and it was

found that the dry bond strength was relatively good despite the low solid content used [85]. However, the water resistance was found to be very poor. In several studies, KGM has been combined with chitosan, as reviewed in Section 3.2.

Xylan extracted from beech has been suggested as a binder in wood adhesives [94]. Xylan itself does not show sufficient bonding performance, especially regarding water resistance. A combination of xylan with dispersing agents with/without crosslinkers has been studied. The best combination was a water dispersion of xylan and polyvinyl amine that exhibited good bond strength, water resistance, and heat resistance [94].

4. Lignin

Lignin is the third most abundant biological macromolecule and exists in the complex and rigid structure of lignocelluloses [1, 95, 96]. It is present in lignocellulosics including wood, grass, agricultural residues, and other plants [97]. It is a high-molecular-weight aromatic polymer based on phenylpropane units in a densely crosslinked structure. Intimately interspersed in the lignocellulose structure, lignin acts as a “glue” binding cellulose and hemicellulose together, thus providing rigidity and microbial resistance to the cell wall [98].

Chemical modification of lignin has been extensively studied [99]. Lignin in adhesive applications has been actively researched and several papers have been published recently on this topic [14, 15, 100, 101]. The main interest in lignins as adhesives is due to its structural similarity to phenol, suggesting they can be used as substitutes for phenol-formaldehyde (PF) resins [102]. In adhesive research, lignin is often combined with synthetic resins such as PF and/or urea-formaldehyde (UF) resins [103] to decrease cost [104] and formaldehyde emission [105].

Lignin in adhesives have rendered limited commercial success mainly due to the low reactivity toward formaldehyde, or other aldehydes, as a result of its complexity and low number of reactive sites [101]. The low reactivity is a disadvantage in applications where short curing times are desired. To enable utilization in various material applications, the reactivity can be improved by modification [106–108]. Phenolic and aliphatic hydroxyl groups on lignin allow for chemical modifications including esterification, etherification, phenolation, oxidation, reduction, and amination.

Lignin was used without any chemical modifications as a phenol substitute in the synthesis of a resin evaluated for plywood applications [109]. This study involved the replacement of phenol with lignin in a PF resol resin. The effect of the formaldehyde ratio was studied, and the prepared plywoods were found to exhibit very low formaldehyde emissions. In terms of thermomechanical properties, the lignin-based resin was reported to be similar to the PF reference. Organosolv and sulphite lignin were phenolated and used as reactive precursors for wood veneers and particleboards [102]. Wet and dry internal bond strength fulfills European standards for load-bearing boards in humid environments. In a recent study, a lignin-urea-glyoxal (LUG) wood adhesive was prepared in attempt to eliminate the use of formaldehyde from wood-based panels such as plywood [95]. No significant decrease in mechanical strength was observed, when it was concluded that glyoxal is a suitable substitute for formaldehyde in wood adhesives. In the same study, further improvement of physical and mechanical

properties was obtained by adding nanoclay to the LUG resin. Lignin was modified by phenol and used in UF resins [110]. It was demonstrated that the formaldehyde emission from wood panels, bonded with modified lignin-UF resin, was lower compared with commercial UF adhesives. Wood panels were also prepared by using lignin in a UF resin [111, 112]. Prior to the resin preparation, lignin was modified by two different methods, either by a pretreatment with a green ionic liquid (IL), 1-ethyl-3-methylimidazolium acetate, or by glyoxalation, to increase the reactivity [111]. Both modifications resulted in UF resins with improved properties. Panels bonded with IL-modified lignin UF resins were superior, regarding mechanical strength, formaldehyde emission, and gel time. The effect of addition of polymeric 4,4-diphenylmethane diisocyanate (pMDI) liquid to (IL)-treated lignin-urea-formaldehyde resin on the physical and mechanical properties of plywood panels ionic have been investigated [112]. The addition of pMDI enhanced the performance of lignin-UF resins for wood-based panels.

Lignin-based adhesives have been formulated by substituting all phenols with unmodified lignin from corn stover in a PF resin. The mechanical strength of the evaluated adhesive system was similar to a commercial phenol-resorcinol-formaldehyde (PRF) adhesive reference [113]. Different industrial lignins, such as softwood Kraft lignins, have been evaluated in self-binding high-density fibreboards, of which some were found to perform well in dry conditions [114]. Lignin has also been blended with other bio-based polymers such as soybean protein and/or chitosan [32, 115]. Lignin amine was prepared by an efficient two-step process, in which lignin was oxidized through a Fenton oxidation reaction, followed by a reductive amination to yield lignin amine [32]. The soybean protein-lignin amine system exhibited high dry and wet strengths for plywood. The improved properties were attributed to the catechol-like functionalities in the system, mimicking marine adhesive proteins. Laccase-modified lignin, combined with either soybean protein or chitosan, followed by reduction with NaBH_4 was evaluated as cheap and safe adhesive systems [115]. The dry strength of the lignin-chitosan formulation was slightly improved when laccase-treated lignin was used, but the subsequent reduction drastically reduced the bonding strength. The laccase-treated and reduced lignin-soybean protein adhesive exhibited more than half the strength compared with a commercial polyurethane adhesive and showed good water resistance.

5. Tannin

Tannins are polyphenols that exist naturally in the bark of various trees such as mimosa, quebracho or pine [116–118]. Natural tannins are divided into two main classes: hydrolysable tannins and condensed polyflavonoid tannins. Condensed tannins constitute more than 90% of the total production of commercial tannins [119]. Tannins are water-soluble compounds [120], and similar to lignin [121], they are of particular interest in the replacement of phenolic resins owing to their chemical structure, similar to phenolic compounds, as well as the ability to react with formaldehyde [120].

The high reactivity toward aldehydes and other reagents renders tannins both chemically and economically interesting in the production of adhesives and resins [120]. However, the present use of commercial tannins for leather manufacturing [122], and beverages [123] limits their availability for other industrial resins. Despite this, tannins have been the subject of extensive

research, leading to the exploration of a wide range of adhesive applications [14, 101, 124]. Attempts have been made to commercialize tannin-based adhesives with limited success [125].

In a recent study, tannins have been suggested as scavengers for formaldehyde in MF resins. The formaldehyde emission was decreased with the addition of tannin [126]. The effect of addition of tannin in PF and MF resins was also studied, and the observed results were improved water resistance and decreased formaldehyde emission [127].

Tannins have also been used as a substitute for phenols in PF resins with promising results. Good characteristics and low formaldehyde emissions were obtained even though only a part of the phenol was replaced by tannin [116]. Noteworthy, curing agents used to prepare such adhesive systems, e.g., tris(hydroxymethyl)nitromethane, paraformaldehyde, hexamethylenetetramine, may cause formaldehyde emission [128, 129]. A hyperbranched polyamine ester was used as a curing agent together with tannin-glyoxalated Kraft lignin (TGKL) and evaluated as an adhesive [120]. The adhesive was evaluated on plywood and the results showed that the modification improved the water resistance strength of TGKL effectively. In another study, lignin-based aldehydes were combined with a reactive tannin from pine bark and evaluated as adhesive in wood panels. The performance was in accordance with relevant standards [130].

Boric acid (BA), a weak Lewis base, is known to induce tannin gelation [131]. Hexamine was used in tannin-BA adhesive systems to fixate BA through complexing onto the network, thus preventing leaching of BA. It is also reported that this treatment enhanced biological resistance [132]. Tannin has been explored for plywood applications by incorporating BA into the adhesive system to increase the hardening rate, thus decreasing press time [133]. The adhesive system was composed of quebracho tannin, NaOH, hexamine, BA, and polymeric isocyanate (pMDI). The results indicated that the addition of BA not only lowered time and temperature of hardening, which is of significant importance for the cost of production of wood composites, but also resulted in higher elastic modulus and good resistance to fungal attack.

Recently, tannin adhesives have also been studied in the preparation of particleboards [122, 134, 135]. Internal bond (IB) strengths of the particleboards were investigated with different tannin-based adhesive formulations [122]. It is reported that particleboards manufactured with the formulation containing paraformaldehyde powder as a hardener exhibited the best IB strength. A formaldehyde-free adhesive based on tannin for manufacturing of particleboards has also been developed [134]. The effect of type and concentration of hardeners was investigated. Tris(hydroxymethyl)nitromethane (TRIS), glyoxal (GLY), and hexamethylenetetramine (HEX) were used as hardener instead of formaldehyde. Condensed chestnut-shell tannins could be combined with low proportions of chestnut bur or eucalyptus bark without reducing board quality. The formaldehyde emission level was low.

Glulam from three layers of lamina has been manufactured by using a mahogany tannin-adhesive system, composed of tannin extract and formaldehyde [124]. The results showed that the adhesive was on par with the conventional adhesive for glulam manufacturing regarding mechanical and physical properties, and had low formaldehyde emission. In a more recent study [136], an adhesive of mimosa tannin, mixed with the *Eremurus* root (syrsh), was prepared to manufacture three-layer particleboards, yielding a fully green product. The addition of syrsh improved the overall performance of the mimosa tannin adhesive system.

6. Outlook

The industry's transition to fully green wood adhesives, i.e., based solely on sustainable bio-polymers, will most likely linger for quite some time. Still, substantial challenges remain to develop bio-based adhesives that fulfill all the prerequisites for both indoor and outdoor applications. Water resistance is one area that is particularly challenging; the general, inherent hydrophilic character of most bio-polymers has to be tampered in such a way that the final adhesive bond is able to withstand both humidity and water sufficiently. There are already promising solutions on how to tackle this, but so far it has almost only been demonstrated on a lab scale and not for large-scale productions. Bio-polymers are also encompassed with large natural variations (molecular weight, solubility, etc.) as an effect of shifting growth conditions which bring about a need for a greater flexibility in the production line, either when manufacturing the adhesive or when conducting the actual bonding. On a lab scale, this is usually manageable but it rapidly becomes a problem when targeting large-scale manufacturing. However, there is light in the tunnel. Hybrid adhesive systems, partly composed of bio-based polymers, already exist and suggest that the transition to greener adhesive systems will occur gradually. Stricter legislations and tougher social expectations are believed to accelerate this development. It is, however, challenged by manufacturers' and end-users' unwillingness to pay more for a greener adhesive, when the transition has to be justified by a neutral cost performance and/or improved final properties. For researchers around the world, the field of green adhesives is an exciting area to be active in. Fundamental research is still required in order to develop detailed understanding of the complex adhesion mechanisms that govern strong bonding between adhesive and substrates. A better understanding will propel the future design of green adhesive systems, and scientific breakthroughs may have a substantial impact on a large industrial sector.

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