

We are IntechOpen, the world's leading publisher of Open Access books Built by scientists, for scientists

6,900

Open access books available

186,000

International authors and editors

200M

Downloads

Our authors are among the

154

Countries delivered to

TOP 1%

most cited scientists

12.2%

Contributors from top 500 universities



WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index
in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?
Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected.
For more information visit www.intechopen.com



Applications of Tannin Resin Adhesives in the Wood Industry

Xiaojian Zhou and Guanben Du

Abstract

Tannin is extracted from natural sustainable materials. It is widely used to prepare tannin resin adhesives owing to its naturally occurring phenolic structure. This chapter aims to introduce the resources and structures of tannin, existing reactions that are involved in the synthesis of tannin resin, and the applications of tannin resin adhesives in the wood industry. Additionally, the advancements in the research based on the use of tannin resins in manufacturing plywood, particleboard, wood preservation, decoration paper impregnation, structural glulam, impregnated fibers, and other wooden products are reviewed. Herein, the main limitations encountered during the application of tannin resin adhesives and the future key research points are identified. Finally, the potential applications of tannin resin adhesives in the wood industry have been discussed.

Keywords: tannins, resins, adhesives, wood industry, applications

1. Introduction

The use of adhesives dates back to approximately 3000 years ago. Several types of adhesives based on specific applications have been developed, particularly for the manufacturing of wood and paper products, among other products. Therefore, thousands of adhesive products have been developed. Factors that affect the selection of the adhesives are cost, assembly process, bonding strength, and durability.

The fabrication of wood-based panel products involves a “preparation and recombination of wood unit” process wherein wood adhesives play a crucial role. Adhesives play a vital role in wood processing because their quality has a direct impact on the performance of the final wood product.

Synthetic and natural resins are the most commonly used adhesives in the wood industry. Some examples of synthetic resins are urea-formaldehyde resin; phenolic resin; melamine formaldehyde resin; and copolycondensation resin, which include phenol-urea-formaldehyde resin (PUF) and melamine-urea-formaldehyde resin (MUF). Some examples of natural resins are soy protein adhesive, tannin resin, lignin adhesive, and starch adhesive.

Although synthetic resin has high weathering resistance and mechanical strength, its raw materials are derived from nonrenewable petrochemical products that are volatile and expensive. Additionally, these products emit formaldehyde, which is toxic and carcinogenic.

The awareness of environmental protection and personal health has been emphasized in recent years. Therefore, natural resins with renewable resources as the main materials have attracted considerable amount of attention. Research

and application of the tannin resin have been highly successful in some countries because its phenolic structure enables its use as adhesives and as a partial or complete substitute for phenols in adhesives. This chapter provides a comprehensive discussion of the situation of the existing tannin resources, reaction mechanisms involved in the synthesis of tanning resins, and general application of tannin resins in the wood industry. This information could provide ideas for the scholars and broaden the application scope of tannin resins in the wood industry.

The production of tannin for leather manufacturing peaked immediately after World War II and has progressively declined. Tannin adhesives were first successfully commercialized in South Africa in the early 1970s. Subsequently, mimosa tannin adhesives were used instead of synthetic phenolic adhesives to manufacture particle-board and plywood for external and marine applications. Tannin resin adhesives have been used in Australia, Zimbabwe, Chile, Argentina, Brazil, and New Zealand [1].

2. Tannin resources

Tannins are extracted from agroforestry biomaterials, such as wood, bark, leaves, and fruits, by the water extraction method. Tannins can be categorized as hydrolyzable tannin or condensed polyflavonoid tannin. The latter is one of the main objects of wood adhesive research and accounts for 90% of the global tannin output. The annual industrial output of tannin reaches up to 200,000 tons.

The distribution of tannin resources in the world has regional characteristics. For example, black wattle tannin is mainly manufactured in Brazil, South Africa, India, and other countries. Quebracho tannin is mainly manufactured in Argentina. Chestnut tannin is mainly manufactured in Italy and Slovenia. Pine bark tannin is mainly manufactured in Chile and Turkey. Oak tannin is mainly manufactured in Poland. Tannin from grape residues, such as skins and seeds, is mainly manufactured in France. In China, tannin is mainly synthesized from larch, poplar, and acacia bark.

3. Tannin structures

Hydrolyzable tannin comprises different types of unit structures, including gallic, digallic, and ellagic acids (see **Figure 1**), as well as sugar esters, which usually exist in the form of glucose [2, 3].

Condensed tannin comprises monoflavonoids or flavonoid units that have undergone various degrees of polymerization. These units are associated with their precursors, such as flavanes-3-ol and flavanes-3,4-diol, among other flavonoids [4, 5]. Each flavonoid contains two types of phenolic nuclei, which are A- and B-ring, as shown in **Figure 2**. The A-ring includes resorcinol and phloroglucinol, whereas the B-ring includes pyrogallol and catechol, among other rare phenols. The A-rings of different tannins possess different chemical structures. The A-rings of tannins extracted from mimosa/wattle, quebracho, Douglas fir, and spruce include resorcinol, whereas those of pine include phloroglucinol.

The main polyphenolic pattern is represented using flavonoid analogs that are based on the resorcinol A-ring and pyrogallol B-ring (I type in **Figure 3**). This unit structure accounts for 70% of tannin. Unit structure II constitutes 25% of tannin and comprises a resorcinol A-ring and catechol B-ring (II type in **Figure 3**). The remaining 5% is a mixture of phloroglucinol-pyrogallol (III type in **Figure 3**) and phloroglucinol-catechol (IV type in **Figure 3**) flavonoids. These four patterns constitute 65–80% of mimosa bark extract. The remaining components are non-tannins,

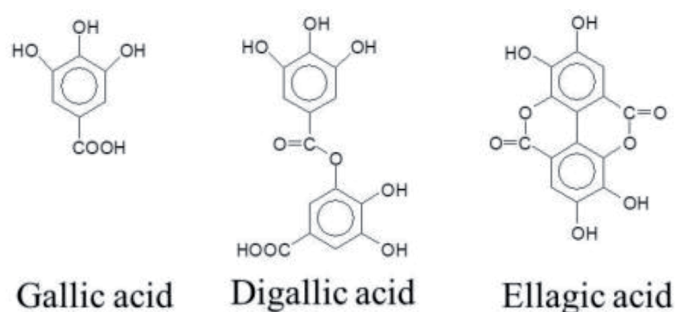


Figure 1.
 Unit structures of hydrolyzable tannin.

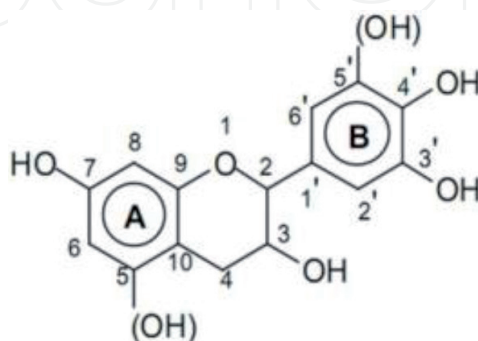


Figure 2.
 Main structure of condensed tannin.

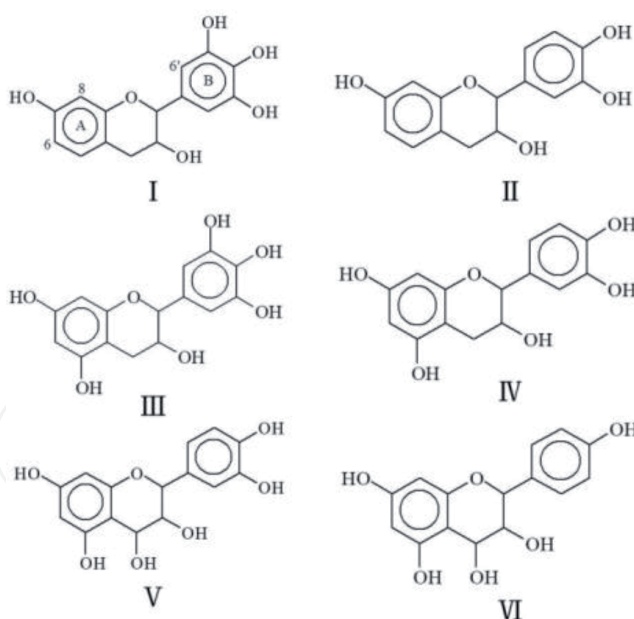


Figure 3.
 Main units of condensed tannin.

which are simple carbohydrates, hydrocolloid gums, and nitrogen compounds, i.e., amino and imino acids. Gums and pectins are the most important components of tannins and have a significant effect on the viscosity of the extract despite their low concentration, i.e., 3–6%. These non-tannin substances can attenuate wood failure and can decrease the water resistance of glued products.

Pine tannin mainly presents two patterns: one is represented by phloroglucinol A-ring and catechol B-ring structures (V type in **Figure 3**) and the other is represented by phloroglucinol A-ring and phenol B-ring structures (VI type in **Figure 3**).

Flavonoid units can be bound through their 4,6- and/or 4,8-linkages to form polyflavonoids. Wattle-extracted tannin comprises 4–5 flavonoid units joined together through 4,6-linkages. Each unit of wattle-extracted tannin has an average mass number of 1250. The average mass number of quebracho tannin and pine is 1784 and approximately 4300, respectively. Pine tannin is phloroglucinolic in nature and its flavonoid units are joined together through 4,8-interflavonoid linkages. Linear polymeric tannins have only 4,6- (V) or 4,8-linkages (VI). However, 4,6- and 4,8-linkages may simultaneously exist in the presence of resorcinolic and phloroglucinolic A-rings. This phenomenon results in the synthesis of angular rather than linear polymeric tannins (VII). Matrix-assisted laser desorption/ionization time-of-flight revealed that mimosa tannin is highly branched owing to the presence of high proportions of angular units in its structure. On the contrary, quebracho tannin is almost completely linear. These structural differences contribute to the considerable differences in the viscosity of tannin water solutions [6].

4. Synthesis of tannin resin adhesives

The low reactivity of hydrolyzable tannins with formaldehyde limits their application in the wood industry, which can be attributed to their simple phenolic structures (**Figure 1**).

Tannin extracts usually contain sugars and gums, which are not involved in the synthesis of resin adhesives. Commercially available tannin extracts from black wattle and hardwood typically contain 70–80% of natural phenolic polymers, whereas those obtained from pine contain only 50–60% of natural phenolic polymers. Sugar dilutes the actual solid content, thus affecting the final properties of resins. Gum considerably affects the strength of the resin and water resistance of the adhesive. Due to the presence of non-tannin components, unmodified tannin adhesive is unsuitable for the production of wood products with high requirements. Therefore, tannin adhesives must be modified.

Normally, the viscosity of tannin resin adhesives is higher than that of synthetic resins at the same concentration due to (1) the presence of high molecular weight tannins in the extract and (2) the existence of hydrogen bonding and electrostatic interactions between tannin and tannin, tannin and gum, and gum and gum. Effective methods for decreasing the viscosity of tannin extracts in aqueous solutions include the following: (1) acid or alkaline hydrolysis of high molecular weight carbohydrates, e.g., with acetic anhydride, maleic acid anhydride, or NaOH [7, 8]; (2) addition of small amounts of hydrogen bond breakers (e.g., 3% urea based on the solid content of the extract); and (3) destruction of heterocyclic ether in tannin molecules through sulfite or bisulfite treatment.

4.1 Reaction of tannin with aldehyde

Tannin being phenolic in nature undergoes the same alkali- or acid-catalyzed reaction with formaldehyde experienced by phenols. Alkali-catalyzed reactions are predominantly used in industrial applications. Nucleophilic centers on the A-ring of any flavonoid unit tend to be more reactive than those on the B-ring. Thus, the reaction for inducing polymerization between formaldehyde and tannin mainly occurs on the A-ring through methylene bridge linkages. The A-ring of the condensed tannin molecules contains flavonoid units that possess one highly reactive nucleophilic center each. The reactivity of the resorcinol A-ring (e.g., wattle) toward formaldehyde is comparable with that of resorcinol. On the contrary, the phloroglucinol A-ring (e.g., pine) behaves as phloroglucinol. Pyrogallol or the catechol B-ring are

unreactive and may only be activated via anion formation at a relatively high pH [9, 10]. Hence, the B-ring does not participate in polymerization except at a high pH (pH = 10). However, the reactivity between the A-ring and formaldehyde influences pot life because it is too fast to control.

In general, only the A-ring structure participates in crosslinking to build networks in tannin resin adhesives (**Figure 4**). However, owing to their size and shape, tannin molecules become immobile at low levels of condensation with formaldehyde. Thus, a large distance between the available reactive sites for further methylene bridge formation results in the incomplete polymerization of tannin resin adhesives. Incomplete polymerization, in turn, results in the formation of weak and brittle adhesives. Bridging agents with long molecules, such as phenolic and amino-plastic resins [10, 11], have been used to overcome this limitation by bridging the distances that are too large for interflavonoid methylene to bridge.

Catechol and catecholic B-ring do not react with formaldehyde at a pH value less than 10. Adding zinc acetate to the reaction mixture induces the B-ring to react with formaldehyde at low pH values, the optimum pH being in the range of 4.5–5.5, as shown by the high amount of formaldehyde being consumed. This finding implies that the further crosslinking of the tannin-formaldehyde network could be achieved through the participation of the B-ring in the reaction in the presence of zinc acetate. Strength can be improved through the addition of zinc acetate at economically acceptable levels (5–10% in resin solids). Nevertheless, improved strength is not comparable with the strength of fortified tannin resin.

Crosslinking is sometimes performed through the addition of isocyanate. The highly reactive diphenylmethane diisocyanate (MDI) can be used to assist the participation of B-ring in the crosslinking reaction [12]. Additionally, the reaction between polymeric diphenylmethane diisocyanate (pMDI) and carbohydrates or hydrocolloid gums can help in increasing the bonding strength of wood products. The reaction rate of wattle and pine tannins with formaldehyde is slowest in the pH range of 4.0–4.5 and 3.3–3.9, respectively.

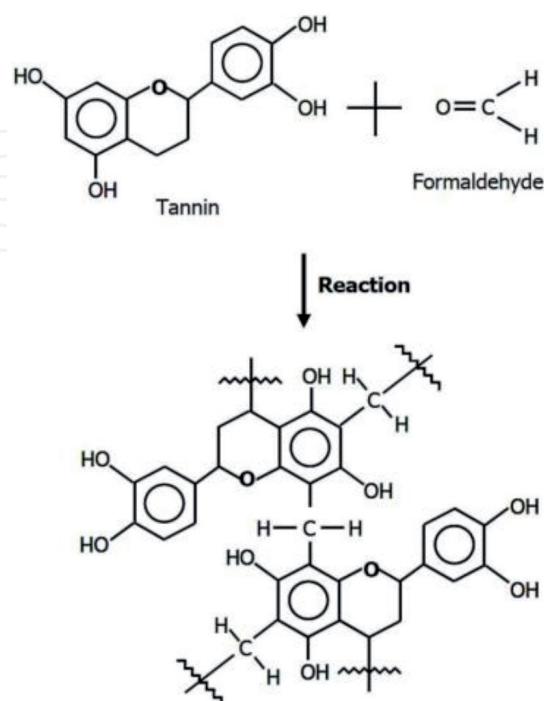


Figure 4.
 Reaction mechanism of tannin with formaldehyde.

Formaldehyde is a major aldehyde used for the synthesis, setting, and curing of tannin resin adhesives. It is normally used as a liquid formalin solution or in the form of the polymer paraformaldehyde, which is capable of fairly rapid depolymerization under alkaline conditions. The formaldehyde reaction with tannin can be controlled by the addition of alcohols to the system. Under these circumstances, some of the formaldehydes are stabilized by the formation of hemiacetals, such as the formation $\text{CH}_2[\text{OH}][\text{OCH}_3]$, if methanol is used. When the adhesive is cured at an elevated temperature, the alcohol is driven off and formaldehyde is progressively released from the hemiacetal. These effects minimize formaldehyde volatilization when the reactants reach curing temperature and extend the pot life of the adhesive.

Hexamethylenetetramine (hexamine) may also be added to tannin resins owing to its formaldehyde-releasing action under heat. Although hexamine is unstable in acidic environments, formaldehyde is liberated under alkaline conditions when heated. This effect indefinitely extends pot life at the room temperature. However, in most cases, hexamine does not decompose formaldehyde and ammonia in the presence of chemical species with highly reactive nucleophilic sites, such as melamine, resorcinol, and condensed flavonoid tannins. Instead, unstable intermediate fragments can be reacted with highly reactive nucleophilic sites, such as tannin or melamine, among others, to form amino methylene bridges before yielding formaldehyde. Any species with a strong negative charge under alkaline conditions can react with the intermediate species formed by the decomposition of hexamine far more readily than formaldehyde. This characteristic accounts for the capability of wood adhesive formulations based on hexamine to render bonded panels with extremely low formaldehyde emission [13].

In the absence of highly reactive species with strong negative charges, hexamine decomposition proceeds rapidly and results in formaldehyde formation. Formaldehyde emissions from wood particleboards bonded with pine and wattle tannin-based adhesives with paraformaldehyde, hexamine, and tris(hydroxyl)nitromethane hardeners have been measured using the perforator method. All particleboards manufactured using wattle tannin systems with three different hardeners satisfied grade E1 requirements. On the contrary, only particleboards made with pine tannin and hexamine hardener satisfied grade E1 requirements. This tendency was attributed to the curing mechanism of the hardener, the reactivity of the tannin molecule toward formaldehyde, and rapid reactivity of pine tannin toward formaldehyde [13, 14].

Formaldehyde is substituted with other aldehydes given that the methylene linkages may be too short to form cross-linkages. Pizzi and Scharfetter have shown that furfural-aldehyde is an efficient cross-linking agent and an excellent plasticizer for tannin resin adhesives [15, 16]. The complete replacement of formaldehyde with other aldehydes is unfeasible owing to their slow reactivity with tannins. For example, the water resistance of cured tannin-formaldehyde networks was improved by substituting 10–30% of formaldehyde with other aldehydes with saturated hydrocarbon chains but not by the cosmetic addition of water repellents such as waxes. Tannin adhesives prepared and/or set and/or cured with other adhesives only or with mixtures of formaldehyde and high proportions of other aldehydes yielded cured bonds weaker than those obtained with formaldehyde alone or its mixtures with furfural.

The metal ion effect on phenol-formaldehyde reactions can be applied to condensed tannins of the flavonoid type with some degree of success. The acceleration effect of the metal ions follows the order of Pb^{II} , Zn^{II} , Cd^{II} , Ni^{II} > Mn^{II} , Mg^{II} , Cu^{II} , Co^{II} > Mn^{III} , Fe^{III} \gg Be^{II} , Al^{III} > Cr^{III} , Co^{III} .

4.2 Acidic and alkaline hydrolysis and autocondensation

Tannin is subjected to two competing reactions when heated in the presence of strong mineral acids: (1) degradation leading to anthocyanidin and catechin formation and (2) condensation as a result of the hydrolysis of heterocyclic rings (p-hydroxybenzyl ether links). The created p-hydroxybenzyl carbonium ions condense randomly with nucleophilic centers on other tannin units to form phlobaphenes. Other modes of condensation such as free radical coupling of B-ring catechol units cannot be excluded in the presence of atmospheric oxygen [17].

The interflavonoid bonds of condensed tannins with phloroglucinolic A-rings are susceptible to cleavage under even mild alkaline conditions. This characteristic could increase the reactivity with aldehydes. Increased reactivity and autocondensation can be introduced through heterocyclic ring opening.

A drastic increase in the reactivity can be attributed to the liberation of the phloroglucinol species of intermediate products. Model compounds have been used to demonstrate that alkaline-catalyzed rearrangements increase tannin reactivity. Nevertheless, some researches have considered model compounds to demonstrate that tannin structural rearrangements can increase or decrease reactivity toward aldehydes.

The autocondensation reactions that are characteristic of polyflavonoid tannins have recently been utilized in adhesive preparation processes, i.e., adhesive hardening in the absence of aldehyde. Autocondensation reactions are based on the opening of the O1–C2 bond of the flavonoid repeat unit and the subsequent condensation of the reactive center formed at C2 with free C6 or C8 sites of a flavonoid unit on another tannin chain under alkaline or acidic conditions (**Figure 5**). Although this reaction increases the viscosity considerably, gelling does not generally take place. Normally, gelling occurs (1) in the presence of a small amount of dissolved silica (silicic acid or silicates) catalyst or some other catalysts and (2) on a lignocellulosic surface.

In the case of highly reactive pine tannin, cellulose catalysis is sufficient to induce hardening and to produce boards with strengths that satisfy the relevant standard requirements for interior-grade panels. The addition of dissolved silica or silicate catalyst to low-reactive tannins, such as mimosa and quebracho, is the best approach to achieve the required panel strength. The amount of silicic acid or silicates affects gelling. Gelling accelerates as silicate content increases and stabilizes after reaching a certain value. Although tannin resin adhesive that was manufactured through autocondensation increases the dry strength of panels, the strength of the resulting crosslinking is insufficient for exterior-graded panels [18]. Aldehyde curing agents should be added for the preparation of exterior-graded panels. Nevertheless, hardening through tannin autocondensation without any aldehyde addition is also possible. The mechanism of polyflavonoid autocondensation has been examined using carbon-13 nuclear magnetic resonance and electron-spin resonance spectroscopy, among others [19–21].

Zinc acetate also appears to induce a similar type of autocondensation reaction that is slower than that induced by an aldehyde. The reaction induced by zinc acetate mainly occurs at high curing temperatures. Consequently, the effect of zinc acetate is too weak to hinder interflavonoid bond cleavage and pyran ring opening in procyanidins. Therefore, in the presence of zinc acetate, the autocondensation of prodelphinidins to prodelphinidins and prodelphinidins to procyanidins will occur, whereas that of procyanidins to procyanidins will never or will rarely occur [22].

The autocondensation of polyflavonoid tannin is facilitated by the reaction that occurs on cellulose and lignocellulosic substrates. Cellulose-induced polyflavonoid

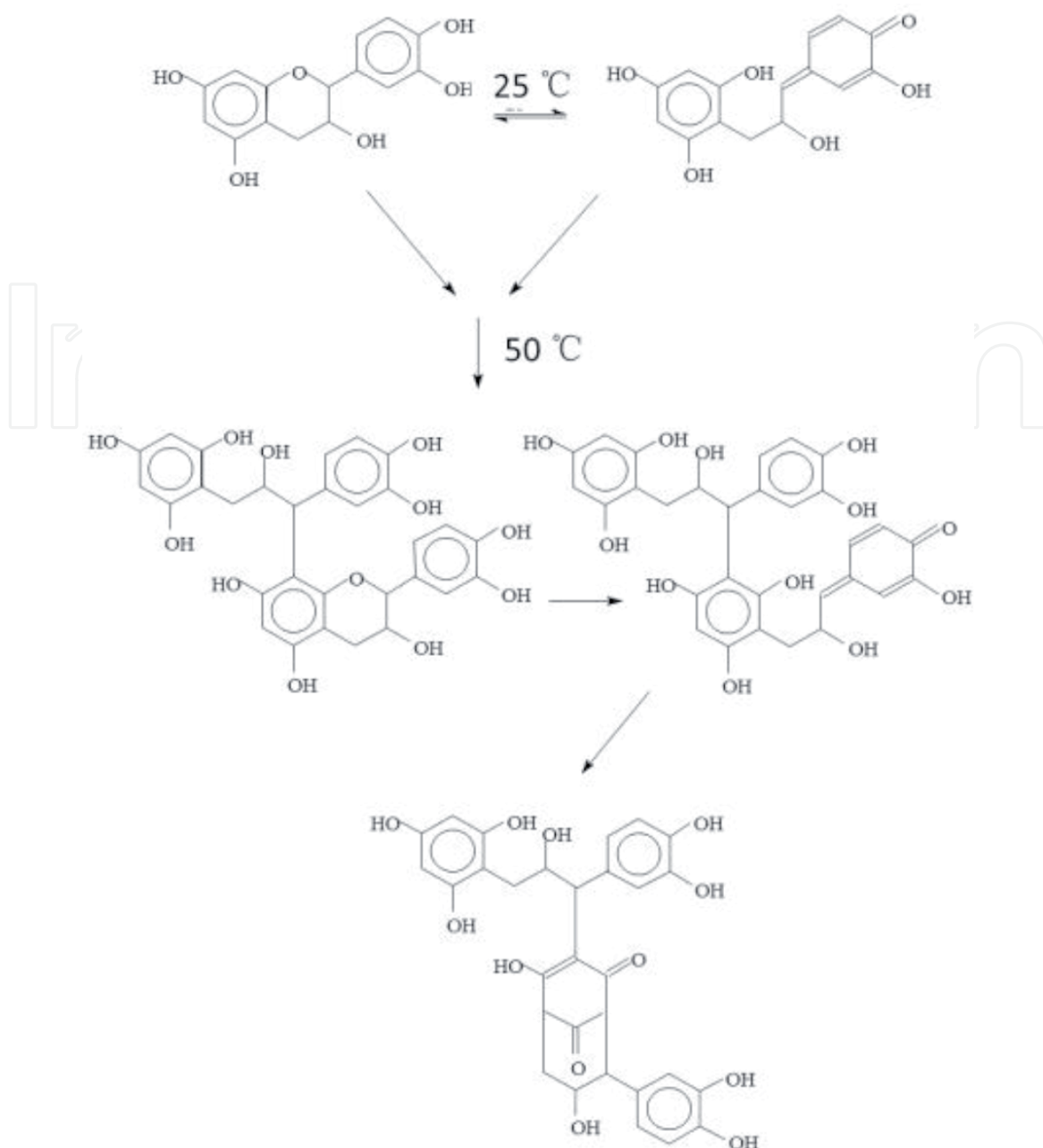


Figure 5.
Autocondensation of tannin resin.

autocondensation and Lewis acid-induced polyflavonoid autocondensation have different mechanisms but involve similar subsequent reactions [23].

4.3 Sulfite reaction

Tannin sulfonation is one of the most useful reactions in flavonoid chemistry and can be particularly useful for the preparation of tannin resin adhesives. The drastic differences between the sulfite treatment products of resorcinol A-ring type tannins (e.g., black wattle tannins) and those of resorcinol A-ring type tannins (e.g., pine tannins) are mainly attributed to the different stabilities of the linkage bonds between their units relative to those of heterocyclic ether bonds. When sodium bisulfite is used to treat black wattle tannins, heterocyclic ether bonds first open because of the relative stability of the connecting bonds between units. Then, sulfonate is added to C-2. In this situation, tannin molecules are negligibly degraded.

The reaction of 5,7-dihydroxy proanthocyanidins with sulfite ions under normal pH conditions proceeds through the cleavage of the interflavonoid bond with the formation of flavan-4- or proanthocyanidin-4-sulfonates, as indicated by the scheme shown in **Figure 6**.

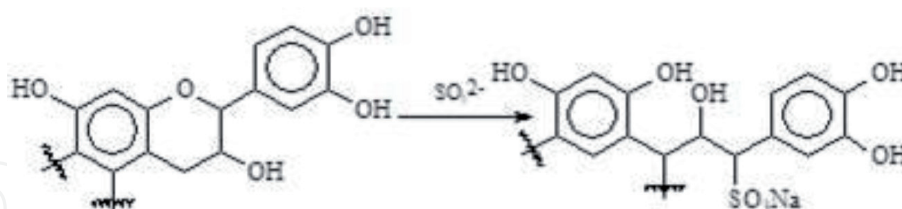


Figure 6.
 Sulfonation of tannins.

Sulfonated products can be obtained from phloroglucinolic tannins without the opening of the etherocyclic ring because interflavonoid bonds are easily cleaved. Flavan-2,4-disulfonates are also formed readily.

The involvement of interflavonoid bond cleavage in the sulfonation of phloroglucinolic condensed tannins affects the utilization of these tannins because their molecular weights can be tailored to suit their applications such as wood adhesives. Additionally, sulfonation affords tannins with reduced viscosity and increased solubility through the following mechanisms:

1. The elimination of the water-repellent etherocyclic ether group.
2. The introduction of the hydrophilic sulfonate group and another hydroxyl group.
3. The reduction in polymer rigidity, steric hindrance, and intermolecular hydrogen bonding through the opening of the etherocyclic ring.
4. The hydrolysis of hydrocolloid gums and interflavonoid bonds under acidic conditions.

However, sulfonation may be disadvantageous because sulfonate groups promote sensitivity to moisture and thus aggravate the deterioration of adhesive. This problem could be solved through desulfonation. The desulfonation of 2,4,6-trihydroxybenzyl sulfonic acid and sodium epicatechin-(4 β)-sulfonate is a facile reaction under mild alkaline conditions (i.e., pH > 8.0 and ambient temperature). Hydroxyl benzyl sulfonic acids with resorcinol or phenol functionalities resist desulfonation at a pH value of 12 and a temperature of 90°C. Therefore, sulfonation not only reduces molecular weight while improving the viscosity and solubility of tannin resin adhesives but also prevents sulfonic acid functionalization and affords aldehyde condensation products that are insoluble in water [24].

5. Applications

Tannin resin adhesives can be cured under high heat (thermosetting) or at room temperature (coldsetting) [25]. Thermoset tannin resin adhesives are used in the preparation of plywood, particleboard, wood preservation resin, and impregnated

resin, among other wood composites. Coldset tannin resin adhesives are used to manufacture glulam, laminating veneer lumber, and finger joints.

5.1 Application of thermoset tannin resin adhesives in glued wood products

5.1.1 Plywood

Tannin resin adhesives are used to prepare plywood (**Figure 7**). However, adhesives manufactured with conventional formulations and technology fails to meet the requirements set for the exterior plywood adhesive. Thus, tannin resin adhesives must be modified by mixing them with other synthetic resins or organic or inorganic modifiers and by optimizing resin synthesis parameters and hot-pressing conditions. Additives can effectively solve the problems of tannin resin hydrophobicity and formaldehyde release and can improve the physical and mechanical properties, especially weather resistance, of the final wood products. Plywood products assembled with modified tannin resin adhesives meet the demand of exterior-grade plywood, have better properties than plywood assembled using phenolic resin, and have a certain commercial potential [26–30].

5.1.2 Particleboard

The use of tannin resin adhesives in particleboard production has been accepted in many countries and is used in the manufacturing of industrial particleboard in many countries except in Asian countries. For example, mimosa tannin resin adhesives are used in industrial particleboard manufacture in South Africa and South America (**Figure 8**).

Although tannin resin adhesives have been successfully used for the production of interior and exterior particleboards, the synthesis processes and formulas of tannin resin are drastically different [31]. Generally, tannin resins polymerized with formaldehyde have higher weathering resistance than those polymerized with other nontoxic and nonvolatile aldehydes in accordance with the reactivity of tannin. Particleboards manufactured using tannin resin adhesives with formaldehyde contents that have been partially or completely replaced with acetaldehyde have very low formaldehyde emission or even free from formaldehyde release and have mechanical properties that meet the requirements of interior-grade application [32]. At the same time, particleboards prepared with tannin resin synthesized via an aldehyde-free process can also meet the requirements of interior-grade applications [33]. An appropriate amount of paraformaldehyde or curing agent must be added to increase the weathering resistance of particleboards prepared with tannin resin

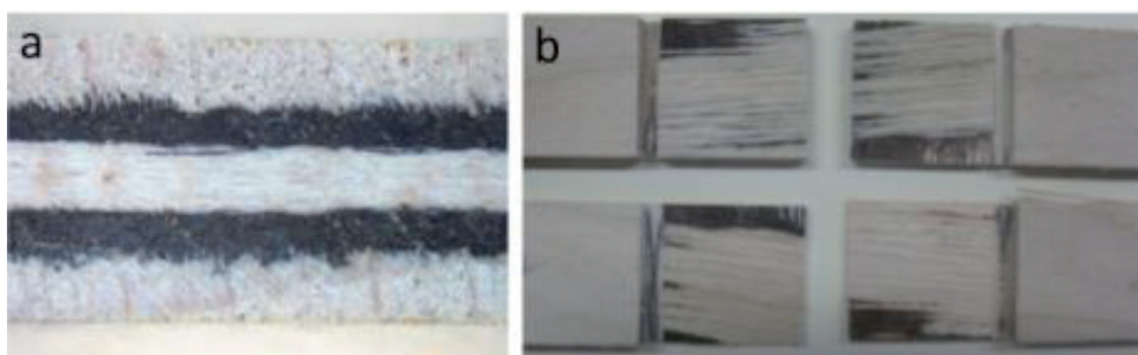


Figure 7.
Tannin resin adhesives for plywood manufacturing: (a) profile image; (b) wood failure.



Figure 8.
Tannin resin adhesives for manufacturing particleboard.

adhesives. Sometimes phenolic resin is also mixed with tannin resin. The properties of particleboards produced with 60% tannin resin still meet the requirements of exterior-grade application [34].

Tannin resin adhesives for particleboard production have high requirements for curing agents. Different types of tannin resin adhesives require different curing agents. The performances of tannin, i.e., tannin structure and curing agent selection, and the properties of the particleboard will be affected by hot-pressing conditions, including pressing temperature, time, and pressure. Selecting an appropriate curing agent can accelerate tannin resin curing, reduce formaldehyde emission, and most importantly, can ensure that the performances of the particleboard meet exterior-grade application requirements [35]. Kim et al. found that the reactive speeds of tannin resin adhesives for black wattle tannin followed the order of paraformaldehyde > hexamine > trinitromethane, whereas those for pine tannin followed the order of hexamine > paraformaldehyde > trinitromethane [36].

Additionally, modified tannin resin can be used to prepare particleboards from different sources, such as wheat straw [37], rice husk [38], cashew nut shell [39], and chestnut shell [40]. The elastic moduli, internal bonding strength, and water-absorbing thickness swelling of the prepared particleboards meet the requirements of European standards.

5.1.3 Wood preservation

Wood preservation is vital for protecting wooden products. Traditional approaches for wood preservation include the treatment of wood with various chemical agents to prevent attack by different organic microorganisms and insects. Although traditional wood preservatives confer good effects and strong durability, they inevitably introduce various other problems, such as environmental pollution and carcinogenic effects. Tannin is a natural fungicide and good preservative that can be used to prevent fungal and bacterial damage [41]. Most plant pathogens secrete enzymes that degrade cellulose and lignin. Tannin can effectively inhibit the activity of these enzymes and prevent the proliferation of pathogens by complexing with protein [42]. Pizzi and Conradie confirmed that the antifungal activity of wood treated with flavonoid tannin resins is twice as intense as that of neat wood [43]. Additionally, veneer treated with tannin resin modified with a small amount of boric acid avoided the fungal attack and exhibited high durability, mechanical strength, and fire resistance because tannin and boric acid can simultaneously inhibit bacterial and fungal growth (**Figure 9**). Meanwhile, the fixation of boric acid in wood with tannin resin and hexamine prevented loss and exerted a good preservative effect that met the requirements of the European standard EN 113 [44–46].

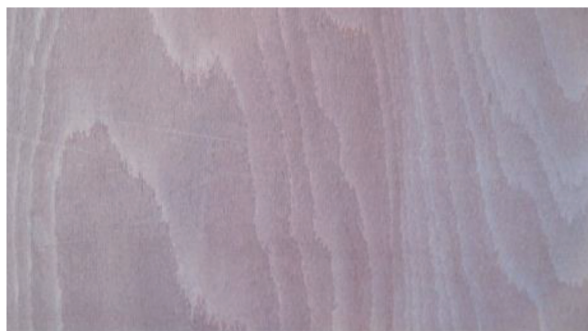


Figure 9.
Tannin resin adhesives for wood preservation.

5.1.4 Wood-impregnated paper

Melamine formaldehyde resin has been widely used in the decorative impregnated paper industry. The addition of small amounts of urea can drastically cut costs without affecting performance. Melamine resin-impregnated paper is widely used for the production of laminated wooden floors and panel furniture overlays [47]. Phenolic resin-impregnated paper has limited applications in the production of floor and furniture panels owing to its black color, but it is widely accepted and popular in some particular applications, such as the impregnation of architectural template veneer paper, owing to its good adhesive property and high strength [48].

The flavonoid phenol structure and properties of tannin are similar to those of phenols. Therefore, there are no theoretical constraints for using tannin resin in paper impregnation. Abdullah et al. [49, 50] synthesized a low-viscosity tannin resin, which was used to impregnate paper with a glue amount of 172 g/m^2 and hot-pressed on wood-based panel substrates. The final overlay paper exhibited a very smooth surface, high wear resistance, scratch resistance, and water steam resistance. The performances of the optimized overlay paper were even superior to those of overlay paper impregnated with MUF resin (**Figure 10**). Similar to phenolic resins, overlay paper impregnated with tannin resin has potential use in template production.

5.1.5 Fiber: veneer composites

Natural fiber composites have been developed to overcome the limitations associated with petrochemical resources. They have extensive prospective applications in the automobile and aerospace industries because their raw materials are derived from biomass and they possess unique characteristics. Fibers impregnated with

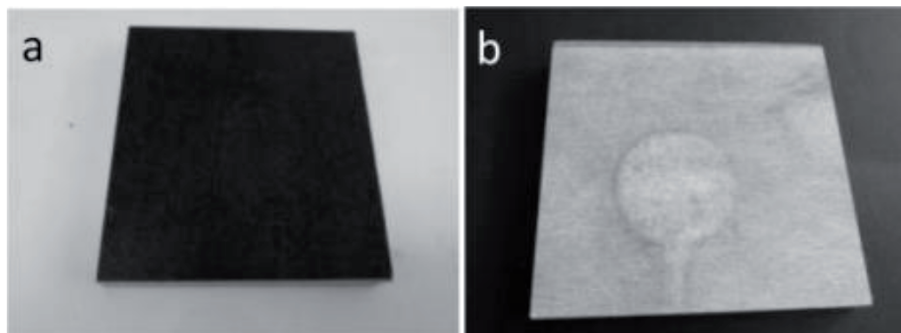


Figure 10.
Overlay paper impregnated with (a) tannin resin; (b) MUF resin.

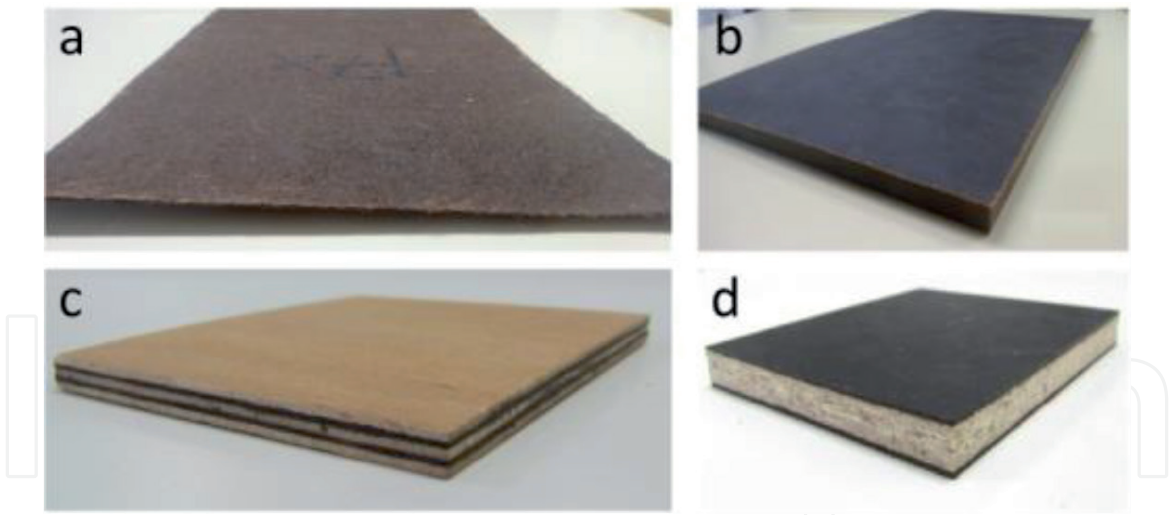


Figure 11.
(a) Tannin resin impregnated fiber; (b) laminated composite with tannin resin impregnated fiber; (c) wood composites with veneer and tannin resin impregnated fiber; (d) tannin resin impregnated fiber overlay on the particleboard.

tannin resin can be used to synthesize different types of fibers or wood-based fiber composites (**Figure 11**). These composites possess high elastic moduli and tensile strength and good water-absorbing expansibility [51–54].

5.1.6 Other wooden panels

In addition to wooden panels, medium density fiberboard [55], oriented strand boards [56], wafer boards [57], container boards [58], and other furniture panels [59] could be prepared with tannin resin adhesives.

5.2 Application of coldset tannin resin adhesives in glued wood products

Adhesives for finger joint lumber and glulam must meet high standard requirements because of the rigorous application environment of these materials (**Figure 12**). These adhesives must possess high mechanical strength and

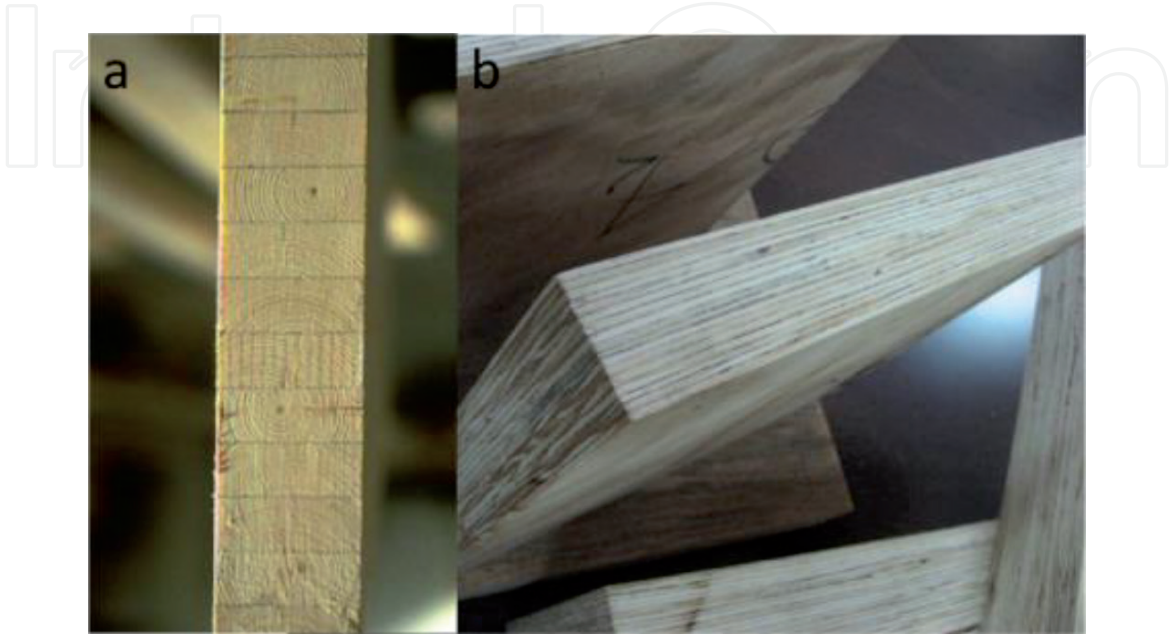


Figure 12.
Coldset tannin resin adhesives for wooden product application: (a) glulam; (b) laminates.

weather resistance. Acacia tree tannin has been widely used to prepare low-temperature curing resin adhesives for finger joint and laminated veneer lumbers [60]. Acacia tannin resin adhesive has a low curing temperature and excellent bonding performance. Additionally, the cost of acacia tannin is lower than that of phenol resorcinol formaldehyde resin. The performance and cost of tannin-resorcinol-formaldehyde resin adhesives must be balanced. The tannin content of such adhesives could reach up to 95% after optimization. The polymerization of resorcinol units is replaced by that of a large number of flavonoid tannin natural phenol units. Resin adhesives with high tannin contents can be cured at room temperature, can exhibit good performances, and can be used to produce veneer and finger joint lumbers and glulam [61, 62]. Other nonvolatile or nontoxic aldehydes, such as glyoxal and glutaraldehyde, are also used to synthesize coldset tannin resin adhesives to effectively reduce the problem of formaldehyde release. Although only a small amount of paraformaldehyde is used to cure tannin resin adhesives, the prepared wooden products demonstrate good mechanical strength and water resistance [63].

6. Conclusions

Tannin has significant application prospects as a promising natural phenolic polymer. However, this raw material continues to exhibit limitations, such as reactivity, high viscosity, short pot life, and poor weather resistance, among others. Future works must address these problems. Research on tannin resin adhesives should focus not only on wood panels but also on other advanced wooden composites. In addition, the industrialization of tannin resin adhesives in the field of wood manufacturing field is necessary.

Acknowledgements

This work is supported by the following grants and programs: 1. National Natural Science Foundation of China (NSFC 31760187); 2. Yunnan Provincial Applied and Basic Research Grants (2017FB060); 3. “Ten-thousand Program”-youth talent support program; and 4. Yunnan Provincial Reserve Talents for Middle & Young Academic and Technical Leaders.

Conflict of interest

There is no conflict of interest in this field.

IntechOpen

IntechOpen

Author details

Xiaojian Zhou* and Guanben Du
Yunnan Provincial Key Laboratory of Wood Adhesives and Glued Products,
Southwest Forestry University, Kunming, China

*Address all correspondence to: xiaojianzhou@hotmail.com

IntechOpen

© 2019 The Author(s). Licensee IntechOpen. This chapter is distributed under the terms of the Creative Commons Attribution License (<http://creativecommons.org/licenses/by/3.0>), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited. 

References

- [1] Dunky M, Pizzl A. Chapter 23–Wood adhesives. In: Adhesion Science & Engineering. 2002. pp. 1039-1103
- [2] Tondi G. Tannin-based copolymer resins: Synthesis and characterization by solid state ^{13}C NMR and FT-IR spectroscopy. *Polymers*. 2017;**9**(6):223
- [3] Roffael E, Dix B, Okum J. Use of spruce tannin as a binder in particleboards and medium density fiberboards (MDF). *European Journal of Wood and Wood Products*. 2000;**58**(5):301-305
- [4] Drewes E, Roux DG. Condensed tannins. XV. Interrelations of flavonoid components in wattle-bark extract. *The Biochemical Journal*. 1963;**87**(1):167-172
- [5] Roux DG, Paulus E. Condensed tannins. VIII. The isolation and distribution of interrelated heartwood components of *Schinopsis* species. *The Biochemical Journal*. 1961;**78**:785-789
- [6] Pasch H, Pizzi A, Rode K. MALDI-TOF mass spectrometry of polyflavonoid tannins. *Polymer*. 2001;**42**:7531-7539
- [7] Pizzi A. Mechanism of viscosity variations during treatment of wattle tannins with hot NaOH. *International Journal of Adhesion and Adhesives*. 1998;**4**(1):213-214
- [8] Sowunmi S, Ebewele RO, Conner AH, et al. Differential scanning calorimetry of hydrolysed mangrove tannin. *Polymer International*. 2000;**49**:574-578
- [9] Pizzi A, Horak RM, Roux DG. Condensates of phenol, resorcinol, phloroglucinol, and pyrogallol as model compounds of flavonoid A- and B-rings with formaldehyde. *Journal of Applied Polymer Science*. 1979;**24**:1571-1578
- [10] Pizzi A. Hot-setting tannin-urea-formaldehyde exterior wood adhesives. *Adhesives Age*. 1977;**12**:27-29
- [11] Pizzi A, Merlin M. A new class of tannin adhesives for exterior particleboard. *International Journal of Adhesion and Adhesives*. 1981;**1**(5):261-264
- [12] Pizzi A. Exterior wood adhesives by MDI crosslinking of polyflavonoid tannin B rings. *Journal of Applied Polymer Science*. 1980;**25**:2123-2127
- [13] Pizzi A, Tekely P. Mechanism of polyphenolic tannin resin hardening by hexamethylenetetramine: CP-MAS ^{13}C -NMR. *Journal of Applied Polymer Science*. 1995;**56**:1645-1650
- [14] Kim S, Kim HJ. Evaluation of formaldehyde emission of pine and wattle tannin-based adhesives by gas chromatography. *Holz als Roh- und Werkstoff*. 2004;**62**:101-106
- [15] Pizzi A, Scharfetter HO. The chemistry and development of tannin-based adhesives for exterior plywood. *Journal of Applied Polymer Science*. 1978;**22**:1745-1761
- [16] Baaka N, Ammar M, Saad MK, et al. Properties of tannin-glyoxal resins prepared from lyophilized and condensed tannin. *Journal of Fashion Technology & Textile Engineering*. 2017;**3**(4):00110
- [17] Sun WD. Chemistry of Tannin. China: China Forestry Publishing House; 1988. pp. 368-388
- [18] Pizzi A, Meikleham N. Induced accelerated autocondensation of polyflavonoid tannins for phenolic polycondensates. II. CP-MAS ^{13}C -NMR of different tannins and models. *Journal of Applied Polymer Science*. 1995;**55**:1265-1269

- [19] Garcia R, Pizzi A. Polycondensation and autocondensation networks in polyflavonoid tannins. I. Final networks. *Journal of Applied Polymer Science*. 1998;**70**:1083-1091
- [20] Masson E, Pizzi A, Merlin M. Comparative kinetics of the induced radical autocondensation of polyflavonoid tannins. II. Flavonoid units effects. *Journal of Applied Polymer Science*. 1997;**64**:243-265
- [21] Garcia R, Pizzi A, Merlin A. Ionic polycondensation effects on the radical autocondensation of polyflavonoid tannins: An ESR study. *Journal of Applied Polymer Science*. 1997;**65**:2623-2633
- [22] Pizzi A, Tekely P. ¹³C-NMR of Zn²⁺ acetate-induced autocondensation of polyflavonoid tannins for phenolic polycondensates. *Journal of Applied Polymer Science*. 1995;**56**:633-636
- [23] Pizzi A, Meikleham N, Stephanou A. Induced accelerated autocondensation of polyflavonoid tannins for phenolic polycondensates. II. Cellulose effect and application. *Journal of Applied Polymer Science*. 1995;**55**:929-933
- [24] Lei H. Résines à base de matériaux naturels et synthétiques destinées aux adhésifs pour le bois. In: Nancy 1. 2009
- [25] Brosse N, Pizzi A. Tannins for wood adhesives, foams and composites: Preparation, Characterization, and Testing. In book: *Bio-based wood Adhesives*. 2017. pp. 197-220
- [26] Efhamisisi D, Thevenon MF, Hamzeh Y, et al. Induced tannin adhesive by boric acid addition and its effect on bonding quality and biological performance of poplar plywood. *ACS Sustainable Chemistry & Engineering*. 2016;**4**(5):2734-2740
- [27] Zhao L, Cao B, Wang F, Yazaki Y. Chinese wattle tannin adhesives suitable for producing exterior grade plywood in China. *Holz als Roh- und Werkstoff*. 1994;**52**(2):113-118
- [28] Moubarik A, Pizzi A, Allal A, Charrier F, Charrier B. Cornstarch and tannin in phenol-formaldehyde resins for plywood production. *Industrial Crops and Products*. 2009;**30**(2):188-193
- [29] Pizzi A, Knauff C, Sorfa P. Effect of acrylic emulsions on tannin-based adhesives for exterior plywood. *Holz als Roh- und Werkstoff*. 1981;**39**(6):223-226
- [30] Gao Z, Yuan J, Wang X. Phenolated larch-bark formaldehyde adhesive with multiple additions of sodium hydroxide. *Pigment & Resin Technology*. 2007;**36**(5):279-285
- [31] Pizzi A. Tannin-based adhesives. *Journal of Macromolecular Science—Reviews in Macromolecular Chemistry*. 1980;**18**(2):247-315
- [32] Ballerini A, Despres A, Pizzi A. Non-toxic, zero emission tannin-glyoxal adhesives for wood panels. *Holz als Roh- und Werkstoff*. 2005;**63**(6):477-478
- [33] Moubarik A, Mansouri HR, Pizzi A, Charrier F, Allal A, Charrier B. Corn flour-mimosa tannin-based adhesives without formaldehyde for interior particleboard production. *Wood Science and Technology*. 2013;**47**(4):675-683
- [34] Lu Y, Shi Q. Larch tannin adhesive for particleboard. *Holz als Roh- und Werkstoff*. 1995;**53**(1):17-19
- [35] Pizzi A, Valenezuela J, Westermeyer C. Low formaldehyde emission, fast pressing, pine and pecan tannin adhesives for exterior particleboard. *Holz als Roh- und Werkstoff*. 1994;**52**(5):311-315
- [36] Kim S, Lee Y, Kim H, Lee HH. Physico-mechanical properties of particleboards bonded with pine and wattle tannin-based adhesives. *Journal*

of Adhesion Science and Technology. 2003;**17**(14):1863-1875

[37] Tabarsa T, Jahanshahi S, Ashori A. Mechanical and physical properties of wheat straw boards bonded with a tannin modified phenol-formaldehyde adhesive. Composites Part B: Engineering. 2011;**42**(2):176-180

[38] Tesha JV, Ndazi B, Bisanda E. Properties of rice husk particleboards bonded by a blend of tannin-cnsl resin. Tanzania Journal of Engineering and Technology. 2018;**25**(2):55-64

[39] Bisanda E, Ogola W, Tesha J. Characterisation of tannin resin blends for particle board applications. Cement and Concrete Composites. 2003;**25**(6):593-598

[40] Santos J, Antorrena G, Freire MS, et al. Environmentally friendly wood adhesives based on chestnut (*Castanea sativa*) shell tannins. European Journal of Wood and Wood Products. 2017;**75**(1):89-100

[41] Zucker WV. Tannins: Does structure determine function? An ecological perspective. The American Naturalist. 1983;**121**(3):335-365

[42] Laks PE, McKaig PA, Hemingway RW. Flavonoid biocides: Wood preservatives based on condensed tannins. Holzforschung-International Journal of the Biology, Chemistry, Physics and Technology of Wood. 1988;**42**(5):299-306

[43] Pizzi A, Conradie W. A chemical balance/microdistribution theory-new CCA formulations for soft-rot control? Material und Organismen. 1986;**21**(1):31-46

[44] Moubarik A, Charrier B, Charrier F, Pizzi A, Allal A. Evaluation of decay resistance of wood products made from borax-impregnated wood and bonded with a formaldehyde-free cornstarch

and tannin adhesive. Annals of Forest Science. 2009;**66**(1):1

[45] Thevenon M, Tondi G, Pizzi A. High performance tannin resin-boron wood preservatives for outdoor end-uses. European Journal of Wood and Wood Products. 2009;**67**(1):89-93

[46] Thévenon M, Tondi G, Pizzi A. Friendly wood preservative system based on polymerized tannin resin-boric acid for outdoor application. Maderas-Ciencia Y Tecnologia. 2010;**12**(3):253-257

[47] Taylor AR, Wulfekotter D. Modified melamine resin for use in decorative laminates: U.S. Patent 4,713,299. December 15, 1987

[48] Chun-gui DU. A study on top grade bamboo-wood composite concrete-form. Wood Processing Machinery. 2004;**15**(1):9-11

[49] Abdullah U, Zhou X, Pizzi A, Merlin A. Note on surface quality of plywood overlaid with mimosa (*Acacia mearnsii*) tannin and melamine urea formaldehyde impregnated paper: Effects of moisture content of resin impregnated papers before pressing on physical properties of overlaid panels. International Wood Products Journal. 2013;**4**(4):253-256

[50] Abdullah UH, Pizzi A, Rode K, Delmotte L, Zhou X, Mansouri H. Mimosa tannin resins for impregnated paper overlays. European Journal of Wood and Wood Products. 2013;**71**(2):153-162

[51] Nicollin A, Li X, Girods P, Pizzi A, Rogaume Y. Fast pressing composite using tannin-furfuryl alcohol resin and vegetal fibers reinforcement. Journal of Renewable Materials. 2013;**1**(4):311-316

[52] Sauget A, Nicollin A, Pizzi A. Fabrication and mechanical analysis of mimosa tannin and commercial

flax fibers biocomposites. *Journal of Adhesion Science and Technology*. 2013;**27**(20):2204-2218

[53] Zhu J, Zhu H, Immonen K, Brighton J, Abhyankar H. Improving mechanical properties of novel flax/tannin composites through different chemical treatments. *Industrial Crops and Products*. 2015;**67**:346-354

[54] Zhou X, Segovia C, Abdullah UH, et al. A novel fiber-veneer-laminated composite based on tannin resin. *The Journal of Adhesion*. 2017;**93**(6):461-467

[55] Xiao-dan H. The development on the black wattle tannin adhesive for exterior medium density fiberboard. *China National Forest Products Industry*. 2003;**30**(5):31-33

[56] Pichelin F, Pizzi A, Frühwald A. OSB adhesives rate of strength development on single strands couples. *European Journal of Wood and Wood Products*. 2000;**58**(3):182-183

[57] Li G, Lei H, Shuang-bao Z, De-rong Z, Qiu-hui Z. Study on tannin resin *Pinus tabulaeformis* waferboard. *Wood Processing Machinery*. 2002;**13**(5):20-23

[58] Saayman HM, Brown CH. Wattle-base tannin-starch adhesives for corrugated containers. *Forest Products Journal*. 1977;**27**(4):21-25

[59] Lee J, Jeon J, Kim S. Green adhesives using tannin and Cashew nut shell liquid for environment-friendly furniture materials. *Journal of Korean Furniture Society*. 2011;**22**(3):219-229

[60] Pizzi A, Rossouw DT, Knuffel W, Singmin M. 'Honeymoon' phenolic and tannin-based fast-setting adhesive systems for exterior grade finger joints. *Holzforschung und Holzverwertung*. 1980;**32**(6):140-150

[61] Gornik D, Hemingway R, Tišler V. Tannin-based cold-setting adhesives for face lamination of wood. *European Journal of Wood and Wood Products*. 2000;**58**(1):23-30

[62] Mansouri HR, Pizzi A, Fredon E. Honeymoon fast-set adhesives for glulam and fingerjoints of higher natural materials content. *European Journal of Wood and Wood Products*. 2009;**67**(2):207-210

[63] Zhou X, Pizzi A. Tannin-resorcinol-aldehyde cold-set wood adhesives with only formaldehyde as hardener. *European Journal of Wood and Wood Products*. 2013;**71**(4):537-538