Current and Future Challenges of Bio-Based Adhesives for Wood Composite Industries

Haisong Wang, Xiaoyu Gong, and Jingwei Gong

Abstract Traditional trialdehyde adhesives are the most prominent adhesives in wood industry, as well as they are also the main reason for the release of formaldehyde during the use of wood glue products such as wood-based panels. There is a growing demand for adhesives prepared with environment-friendly from biomass materials to transition toward a more sustainable society. The development and application of new promising adhesives not only involve resource reasonable utilization and environmental protection, but also have great significance to the profound development of adhesive industry. In this chapter, the characteristics, preparation technology, modification methods and current research progress of several bio-based adhesives (lignin, tannin, soybean protein and starch) are reviewed, the application status and the existing problems of bio-based wood adhesive are analyzed, and the development direction of bio-based wood adhesives is prospected.

Keywords Bio-based adhesives · Wood composite · Lignin-based adhesives · Tannin-based adhesives · Soybean protein adhesives · Starch-based adhesives

1 Market and Performance Requirements of Adhesives for Wood Composite Industries

1.1 Adhesives for Wood-Based Panels

As one of the largest green economies in recent years, the progress of wood composite industries in the national sustainable development would bring forward a new impetus, particularly the wood-based panel development in industry. Given the environmentally friendly development of forestry, the wood composite is a beneficial method to improve the utilization of wood resources effectively. In 2014, China and

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Indonesia were recognized as the world's most important suppliers of wood-based panels, accounting for more than 55% of total exports. In 2018, the total output of China's wood-based panels reached up 299 million m^3, among which plywood accounted for 60%, and China remained the largest producer of wood-based panels in the world. It also shows that the global wood-based panel market is expected to grow at a compound annual growth rate (CAGR) of more than 3%, exceeding 35 billion dollars by 2023. Due to the continued economic growth in Asia, the recovery of the North American market, and the expansion of bioenergy targets, the production shows great potential to be further explored in the future. With the rapid development of the international wood composite industries, the emergence of adhesives has attracted enormous attention in saving raw materials and simplifying the processing technologies of wood products.

Based on incomplete data, the production of wood adhesives in the world accounts for 50–60% of the total production of adhesives, meanwhile the production of wood-based panel adhesives accounts for more than 80% of the production of wood adhesives. Thereby, it is of advantage to some extent to develop the wood-based adhesives from the perspective of a steady growth of the world economy.

More high requisitions for curing speed, curing temperature and viscidity have been brought forward.

Currently, a variety of adhesives have been developed. Trialdehyde adhesives, accounting for more than 90%, have been widely used in the market. However, environmental pollution, chemical raw materials prices rising and the urgent demand of energy conservation and emission reduction have become a pressing need to explore adhesives with high performance, functionalization green cleaning and non-toxic broadening wood related research to the functional materials. Therefore, bio-based adhesives have become new requirements for wood-based panel manufacturing industries. At present, the main bio-based adhesives for wood-based panel include lignin-based adhesives, tannin-based adhesives, soybean protein adhesives and starch-based adhesives. From the view of a sustainable improvement for synthesis technology, bio-based adhesives are widely used for its remarkable and promising applications in the field of bioscience.

1.2 Wood Adhesives for Decorative

Plywood in the market of decoration industry is not as good as that in the wood composite industry, but its development potential is not underestimated. Currently, the number of populations has increased significantly, and land resources are more and more tight, leading to the buildings have begun to multi-story and high-rise development, so people have higher and higher requirements for building decoration materials with the lightness and high strength characteristics. In today's society where new materials are constantly emerging, the reason why wood materials still play an extremely important role in building decoration is that it has incomparable advantages over other materials, such as irreplaceable natural properties, typical green materials

and excellent physical and mechanical properties. Moreover, in order to take the sustainable development path, building decoration materials has been considered a trend, with green, energy saving, low-carbon and environmentally friendly and the market of building decoration materials is absolutely inseparable from these standards in the future. Only in this way can people's living standard be effectively improved and it is not difficult to foresee that the decoration industry in the world is also a "sustainable resources, evergreen format" industry, and green wood furniture and wood decoration will inevitably become a trend of decoration professions, and the proportion of wood adhesive for decoration will also increase.

Adhesives used in furniture and the secondary processing of wood-based panels have certain requirements on bond strength, endurance and cold resistance. Now the products used in the market are mainly polyvinyl acetate emulsion (PVAc), acrylate emulsion, hot melt adhesive and other adhesives. PVAc could be widely used in the adhesion of porous materials, especially wood composite products because it has fascinating advantages, such as, non-toxicity, safety, and no environmental pollution. However, drawbacks such as poor water resistance, heat resistance and frost resistance still remain. The advantages of acrylate emulsion lie in its wide sources, pollution-free, and simplicity of synthesis. However, how to improve water resistance is attractive but remains challenging. Some scholars have applied the polymer emulsifier to the synthesis of acrylate copolymer emulsion adhesive to improve the water resistance. Hot melt adhesive as a synthetic adhesive, which has accounted for more than 20% of the total production of synthetic adhesives in developed countries, has emerged for the purpose of artificial board surface decoration and wood sealing due to its excellent properties, including pollution-free, large bonding surface, fast bonding speed, suitable for continuous production, easy to storage and transportation, and has contributed to successful development of environmentally friendly adhesives. Natural, ecological, green, healthy and recyclable manufacturing are still the main trends of decorative adhesives in the current world.

2 Recent Developments of Bio-Based Adhesives for Wood Composite Industries

In recent years, petroleum-based products have innumerous uses in various industries for its cheap availability, but it eventually decreases the availability of fossil fuel which will raise the prices of petroleum-based raw materials. To address the issues regarding environmental pollution, we suggest to use natural adhesives for industrial applications. Bio-based adhesives, as a kind of environmentally friendly adhesive with renewable, have given rise to a whole new and green range of uses.

The development of formaldehyde free environment-friendly adhesives by using cheap renewable resources is the research direction of global wood composite industry adhesives. Overall, the materials of adhesives from biomass alternatives

have attracted attention and converting lignin into bio-based adhesives may pave a promising way to substitute petroleum-derived products.

Great potential has been gained in research for past few years, however, bio-based adhesives still have some major disadvantages like high viscosity, low bonding strength and poor water resistance. In this chapter, the research status of lignin-based adhesives, tannin-based adhesives, soybean protein adhesives and starch-based adhesives are discussed.

2.1 Lignin-Based Adhesives

Lignin is the second largest renewable natural resource after cellulose and the only non-petroleum resource of renewable aryl compounds in nature. The annual yield of 6×10^{14} t worldwide makes lignin the largest natural polyhydroxy aromatic compound. Besides, lignin is also the primary byproduct of pulp and paper industries. Of these, cooking waste liquor is comprised of up to 50 million tons of technical lignin worldwide annually. Structural unit consists of phenylpropane linked together through carbon–carbon bonds and ether bonds forming a three-dimensional network polymer and has been also made into other materials such as emulsifiers, dispersants and polyvalent chelating agents as well as other fields. Meanwhile, as compared to the phenolic resin, lignin has relatively good self-adhesive properties (Fig. 1) and can become the substitute raw material of the phenolic resin adhesives prepared to be extensively applied to the adhesive industries. To some extent, the amount of formaldehyde can be decreased. However, the lignin cannot meet the demands modern society for high performance materials due to high steric hindrance, complex structure, small number of active groups and large resistance of aromatic ring structure. In order to increase the reactivity of lignin, activation modification is often used to increase the content of existing active groups or introduce new active groups, and the molecular weight is reduced to a certain extent, which can be used to fabricate different types of adhesives with high performances.

Because the side chain of lignin macromolecules has hydroxyl groups, ether bonds, double bonds and other groups, the α position of the side chain is an active center. Therefore, phenol and its derivatives can be used to modify lignin, which introduces phenol group in order to improve the content of phenolic hydroxyl. the reactivity of lignin could be improved effectively by the introduction of phenolic hydroxyl group, because of the small size and high activity of phenolic hydroxyl group. A ternary gradual copolymerization approach was reported for the preparation of steam explosion lignin phenol formaldehyde adhesives with excellent performance (Zhao et al. 2016), meanwhile the maximum substitution rate of phenol reached 70 wt% and phenolic hydroxyl content of lignin increased by 130%. Raj et al. (2020) reported that 100% phenolic lignin was utilized for the synthesis of LF resin and evaluated the effect of isolation method on the physicochemical properties of lignin through three different approaches-Alkaline hydrolysis, mild acidolysis and organosolv. The results showed that lignin has unique features and unique properties, such

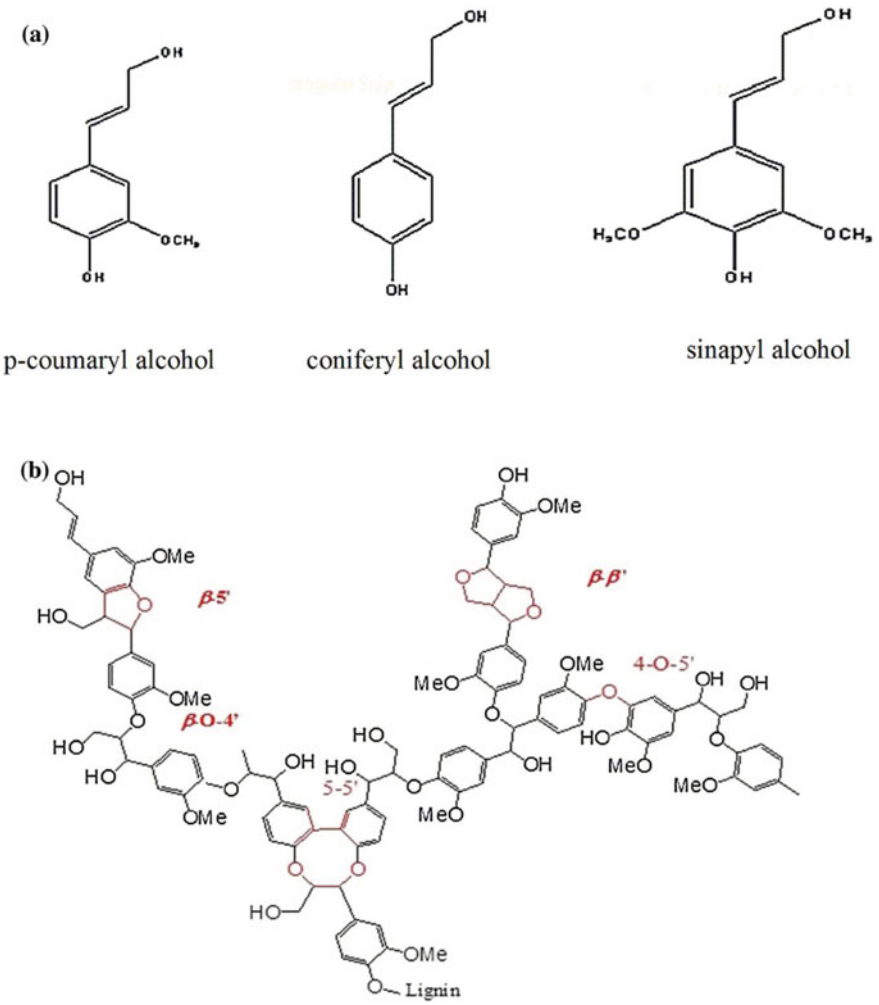

Fig. 1 **a** Three monomers of lignin; **b** Representative connection type of lignin (Naseem et al. 2016)

as a number of G type units of alkali and organic solvent lignin, free ortho-position (C_5) and appropriate molecular weight. These features make lignin suitable in the preparation of adhesives.

With the condition of alkali, the free phenolic hydroxyl group on the benzene ring of lignin reacts with formaldehyde to produce hydroxy methylated lignin by introducing hydroxymethyl groups. Although the active site of lignin might not be increased by hydroxy methylated modification, the introduced hydroxymethyl could

not only copolymerize with phenol or C_5 of lignin structure, but also copolymerized with hydroxymethyl phenol or hydroxy methylated lignin to make the reaction activity easier for improvement. Yang et al. (2015a; b, c) modified lignin by bio-refining technology, hydrothermal degradation, hydroxymethylation and phenol reaction to make it have higher activity and prepare lignin-based adhesive with better performance. Additionally, lignin-based adhesive was demonstrated to be efficient to reduce the emission of formaldehyde (0.11–0.24 mg/L), but bonding strength of plywood was not significantly decreased (1.35 MPa). In addition, in order to circumvent the delamination, plywood was chosen for adhesion because of its high strength, extremely moisture resistance, and excellent temperature stability. Yang et al. (2019) first put forward to add nanosized lignin (LNP) and microlignin (LMP) to phenol–formaldehyde resin adhesive. Given plentiful phenylpropane units and the higher specific surface area, nanolignin has potential to contribute to the cure reaction, and the shear strength of plywood could be enhanced by LNP. Results showed that the shear strength could be increased positively with 5 wt% of LNP, which ranging from 8.7 to 10.9 MPa. It is safer to the environment and can generally lead to the crosslinking of traditional phenol wood adhesives by introducing nanoscale lignin, and resulting in adhesives with favorable adhesion ability (Fig. 2).

Because of the different kinds of wood fiber raw materials, the active C_3/C_5 of the aromatic ring is occupied by the methyl oxygen groups which limits the reaction activity of lignin. Therefore, the demethylation reaction could enhance the reaction

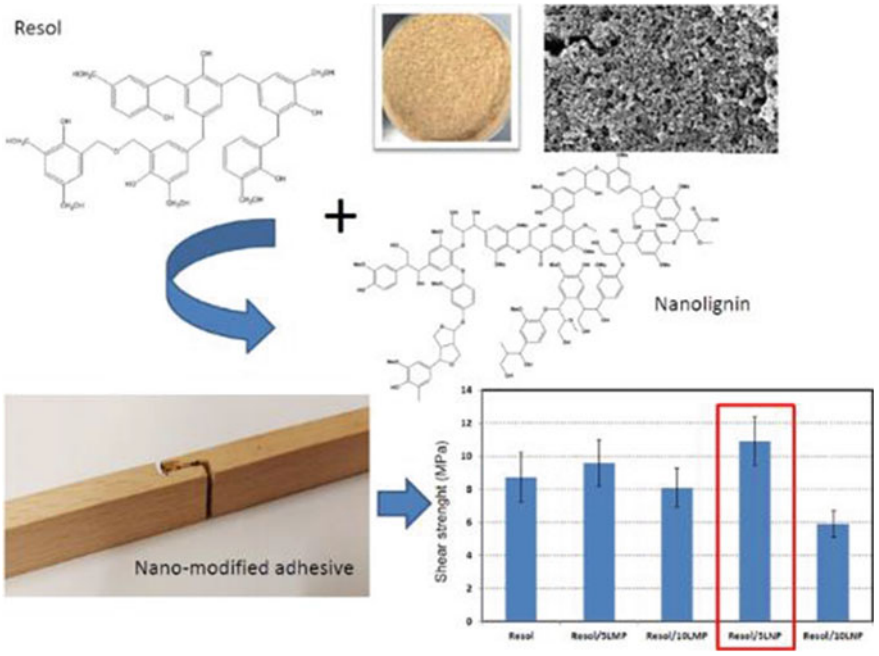

Fig. 2 Reaction diagram of lignin-based adhesives (Yang et al. 2019)

activity of lignin, since the methoxy may be partially or completely converted into phenolic hydroxyl. At present, sulfide demethylation is the most common method for modification of lignin. According to the basic conditions, the process of dismethylation of lignin was used by sulfur, and the results showed that the content of phenolic hydroxyl increased from 3 to 5.6%, the content of methoxide decreased from 12 to 7.6%, and the molecular weight also decreased significantly. In conclusion, the lignin reactivity was significantly improved after modification. Song et al. (2016) used an in-situ generated Lewis acid to demethylate wheat straw alkali lignin. The results showed that the relative content of the phenolic hydroxyl group increased from 5.2 to 16.0%, while the relative value of methoxy group decreased significantly from 0.82 to 0.17% after the demethylation process. Therefore, the demethylated wheat straw alkali lignin was then used to prepare lignin-based phenol formaldehyde adhesives with replacing 60 wt % of phenol, which could open up a new area of applications in the phenol formaldehyde adhesives. Wang et al. (2019) reported that alkali lignin was demethylated with HI and HBr to improve the content of hydroxyl and its reactivity for the phenolic resins preparation. Prepared by copolymerization, lignin-containing resins conformed to the bonding strength standard of external plywood. The demethoxide process not only increased the hydroxyl content but also imparted faster cure times and lower formaldehyde emission of lignin-containing resins. Venkatesagowda and Dekker (2019) studied The dehydrogenation of Kraft lignin (KL) by wood-rot fungi. The O-methyl/methoxyl groups of lignin were removed by demethylation of the action of O-demethylases liberating methanol, and a demethylated KL enriched in vicinal-hydroxyl groups was produced with potential to serve as lignin-based phenol–formaldehyde polymers. Their study clearly revealed the mechanism of lignin demethylation, and it was possible to manifest that the O-methyl/ methoxyl groups had reported similar demethylase activities as model lignin compounds via enzyme activity usually shown by O-demethylases, thus providing critical evidence for the presence of specific fungal enzymes that catalyze such reactions.

In recent years, ionic liquid comprised of anions and cations as a new solvent system can completely dissolve lignin fiber raw materials, greatly promoting the basic researches of lignin conversion and application. In the process of dissolution, lignin can be activated and modified in the state of dissolution of ionic liquid due to its high coordination capacity. Furthermore, lignin could be an excellent candidate for chemical modification material because of its great functionality, low molecular weight and high activity for the development of bio-based materials. Different from other modification methods, it is more advantageous to use lignin modified by ionic liquid to prepare phenolic resin adhesive instead of phenol. The ionic liquid interacts with lignin mainly through hydrogen bond, which is stronger than the interaction between lignin molecules, resulting in lignin dissolves in the ionic liquid. The result suggests that the addition of reverse phase solvent can lead to lignin regeneration (water, ethanol, etc.) (Ji et al. 2012). Younesi-Kordkheili and Pizzi (2017) investigated the physical and mechanical properties of ionic liquid modified lignin-phenol–formaldehyde (LPF) resin, soda bagasse lignin modified by 1-ethyl-3-methylimidazolium acetate ionic liquid plywood, and then, various contents of

modified lignin were added as an alternative for phenol in phenolic-formaldehyde resin (PF). The research results showed that the viscosity and solid content of the synthesized resins increase, while the gel time and density by addition of treated lignin decrease. With the increase of lignin content percentage varying from 0 to 20 wt%., the mechanical properties of the sheet could be significantly improved.

Microwave reaction technology provides unique advantages such as fast heating rate, high heat transformation efficiency and uniform heating, to reduce the activation energy needed for the reaction and vividly improve the reaction rate. Microwave-assisted biomass hydrothermal liquefaction is a thermal decomposition process in the presence of water, where heat can be transferred from the biomass interior to the surface by microwave irradiation. This process of preparing liquid fuels and high value-added chemicals has attracted worldwide attention due to its low cost and short reaction time. These characteristics indicate that microwave-assisted hydrothermal liquefaction may be beneficial to the preparation of lignin-PF products. Li et al. (2017) extracted lignin from bagasse with 93% acetic acid solution and rapidly degraded by microwave in hot compressed water with oxalic acid as catalyst to produce phenolic formaldehyde (PF) adhesives and the molecular weight, viscosity, and adhesive strength of the adhesives were found to be lower than those of pure PF adhesives.

2.2 Tannin-Based Adhesives

The word tannin has been used extensively to define two different types of compounds which are primarily phenolic in nature: hydrolysable tannins and condensed tannins. The former correlated with mixtures of simple phenols, like pyrogallol and ellagic acid, and esters of a sugar, mainly glucose, with gallic and digallic acids. Contrary to it, condensed tannins, accounts for more than 90% of the world's total commercial tannins (200,000 tons per year) and are chemically and economically more suitable for the preparation of adhesives and resins. Tannin is one of the most successful forest resources to be used as wood adhesive consisting of condensed tannin as the main raw material and curing agent, which has fast curing speed, low price and good sizing performance. It has been proven that selecting appropriate curing agent in preparation of wood adhesive is useful for enhancing the time of cold curing and release of free formaldehyde. Tannin molecules are generally composed of 5–11 sulfonanol units. The two phenolic rings (A and B) in the molecule are held together by a heterocyclic ring. As a polyphenolic compound, tannins have a high nucleophilic property of their sulfonanol unit A ring and can react with formaldehyde and finally form insoluble polymers under the action of alkali catalyst, whose principle is the same as that of phenol and formaldehyde reaction to prepare phenolic resin and also has similar adhesive properties and aging resistance to phenolic resin adhesives. Although considerable efforts are still being devoted to extending other applications to tannin adhesives, high molecular weight, high viscosity, low crosslinking degree,

short applicable period and poor physical and mechanical properties are also its main setbacks.

Pizzi team (2006) has had in-depth research on the synthesis and preparation of classic tannin adhesives and been widely used in many countries. The technologies of interest here are the new ones according to the use of hardeners which are either non-emitting or manifestly non-toxic. Two lines of investigation were pursued and their function well as hardeners for a variety of tannin-based adhesives while affording considerable side advantages to the adhesive and to the bonded wood joint. Tannin-modified phenolic resin has some unique features such as high molecular weight, high viscosity, high space resistance, and short production circle. Therefore, it is still very difficult to use concentrated tannins without pretreatment. To address this issue, Liu et al. (2020) carried out the depolymerization of condensed tannins in a mixed aqueous solution of sodium hydroxide and urea. Macromolecular condensed tannins were pretreated with sodium hydroxide/urea solution and depolymerized into small molecule tannins solution. The results showed that the water solution with NaOH/urea = 0.2/0.175 (mol/mol, every 100 g of treatment solution) had a better depolymerization effect on Acacia mangium tannin. With the aim of have a good contribution in innovation of green chemistry, notably, this cheap and environmentally friendly catalyst has been demonstrated to be of great for the synthesis process as a feedstock can be used as a feedstock for the synthesis process; Degradation products do not need to be recovered and purified, which avoids the dehydration and purification of waste liquid and makes it safer for the environment (Fig. 3).

In the wood composite industry, the combination of tannin adhesives and other adhesives may have unexpected effects. Eghtedarnejad and Reza (2015) investigated the possibility of combination of tannin adhesive and natural and renewable adhesive

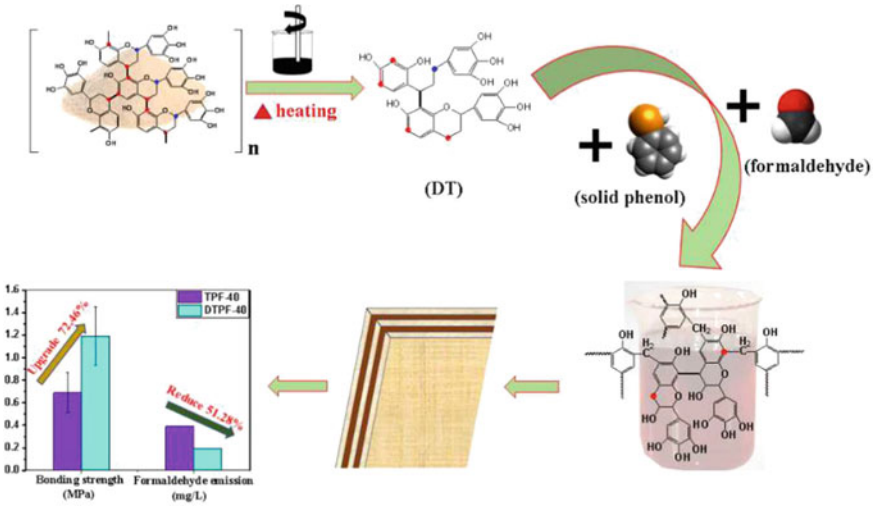

Fig. 3 Degradation mechanism diagram (Liu et al. 2020)

of syrysh and the prepared adhesives were measured to be 35 kg/cm^2 at 210 °C. When the tannin content was 6 + 4%, the level of adhesive resistance was the highest, at 0.89 Mpa. The amount of water absorption and thickness swelling were decreased and reached standard level by increasing the percentage of the dry weight of the syrysh adhesive. For the sake of finding partial substitution for bisphenol A-based commercial epoxy resin (CE), a bio-based epoxy resin was prepared by Shnawa (2020) from eucalyptus tannins via a typical glycidylation reaction with epichlorohydrin. Tannins used here are extracted from the barker of eucalyptus tree and consist mainly of condensed tannins. The tannin-based epoxy resin (TE) can be used as curing accelerator, which has an unsatisfactory effect on curing performance of CE resin, such as curing enthalpy. And up to 20 wt/wt% of CE could be replaced by TE without any significant reduction in the curing behavior of CE. For TE used at 20% loading in the CE, the maximum curing peak is at 116.7 °C and curing enthalpy equals to 127.4 J g^{-1} closed to that of pure CE. In future, the study of chemically modified tannins as unconventional organic fillers prepared by bio-based composites will be a promising perspective. The exploration of mechanical and physical properties of the composites produced has been a subject of environmental interest because of its attractive advantages. Chen et al. (2020) developed a bio-based adhesive from soybean meal and larch tannin that was designed for exterior use. The addition of Phenol hydroxymethylated tannin oligomer (PHTO) in soybean meal-based adhesive decreased the moisture absorption rate of the resultant adhesives, and effectively increased the wet shear strength of the resultant plywood. The wet shear strength and formaldehyde emission of the resultant plywood were 1.04 MPa and 0.08 mg/L, respectively, which both satisfiedthe bonding strength requirements of outdoor plywood and E_0 level. The improvement of adhesion performance was mainly due to the cross-linking structure among PHTO and proteins, as well as the cross-linking of PHTO itself.

2.3 Soybean Protein Adhesives

Protein-based adhesive is a kind of adhesive with protein or its hydrolyzed products, denatured products and plant protein-based adhesives as the main processing by-products of agricultural products. It has abundant sources and good reproducibility, and mainly consists of soybean protein. Soybean with abundant, renewable, inexpensive and easy to obtain have emerged as critical component for the purpose of exploring new composite applications. In the preparation of soy-based adhesives, soybean products are modified by appropriate means to make them have the properties of natural polymer synthetic resins. Finally, a kind of adhesives prepared by adding a series of additives can be directly used in the wood composite industry. Soybean protein is a compound mainly comprised of soybean globulin and soybean whey protein, 90% of which is soybean globulin. Soy globulin has a special spherical structure, so that most of the hydrophobic groups are wrapped in it. Meanwhile,

the impact of exposed hydrophilic groups of soybean protein adhesive on water resistance is considerable.

The modification of soybean protein adhesives is generally modified to improve the mechanical properties of soybean protein adhesives, and it uses biochemical and physical factors to alter amino acid residues and polypeptide chains. Due to the destruction of hydrogen bonds and other chemical bonds, the secondary, tertiary, and quater-level structures are destroyed, which leads to the original irregular bending, folding, and spiral shapes are gradually extended to form a loose linear peptide bond structure, so as to improve the viscosity of the modified adhesive of soybean protein and increase the contact area for adhesive. Meanwhile, the formed soybean protein adhesive should be special structure with the hydrophobic structure inward and hydrophilic outward. The hydrophobic group inside the modified soybean protein will be exposed, which prevents the soybean protein from forming hydrogen bond with water, and then hinder the damage of water to the binding body of the soybean protein adhesive, thus improving the water-resistant property of the soybean protein adhesive. With a small amount of uniform distributed chemical bonds as the backbone core, the resultant force formed together with a large number of hydrogen bonds could be the glue relay source of modified soybean adhesive, which not only guarantees the dry bond strength but also improves the water resistance.

Physical modification to high-level structure and intermolecular aggregation mode of proteins are beneficial under the conditions of high temperature, ultraviolet light, and ultrasonic waves. In the water phase medium, the strong pressure, shear force and high temperature of the protein molecules, the hydrogen bond fracture between the protein molecules, the amino acid is exposed, the soybean protein is trans-modified, the original biological activity is lost, and the solubility of the protein and the strength of the glue are significantly improved. Yang et al. (2010) investigated effects of ultrasonic wave on properties of modified soybean protein adhesives for duplex paper and obtained the optimum conditions by orthogonal experiment as follows. The results showed that treatment temperature had the greatest impact on adhesive strength of soy protein adhesive, followed by urea concentration, protein concentration, treatment time, and ultrasonic time. Apart from ultrasonic, high-pressure homogenization is also a common method of physical modification. Soybean meal (SM), a byproduct of bean oil production, had been alternative formaldehyde-based wood to develop bio-adhesive. However, SM adhesives suffer from drawbacks such as uneven particle size distribution, and hydrophilic hydrogen bonds which result in SM adhesives' low adhesion stability and poor water resistance. To overcome these problems, a stable high-performance bio-based adhesive was developed using a simple, clean and physical high-pressure homogenization (HPH) technology in conjunction with eco-friendly cross-linking by Zhang et al. (2020). Results showed that HPH treatment reduced the SM's particle size by 62%, improved the particle size distribution uniformity, and significantly enhanced bonding stability of the adhesives. Furthermore, many active functional groups within the soy protein were exposed simultaneously during HPH, which increased their reactivity with the cross-linker. Moreover, the method has been successfully applied to industrial production on a pilot scale and has a broad practical application prospect.

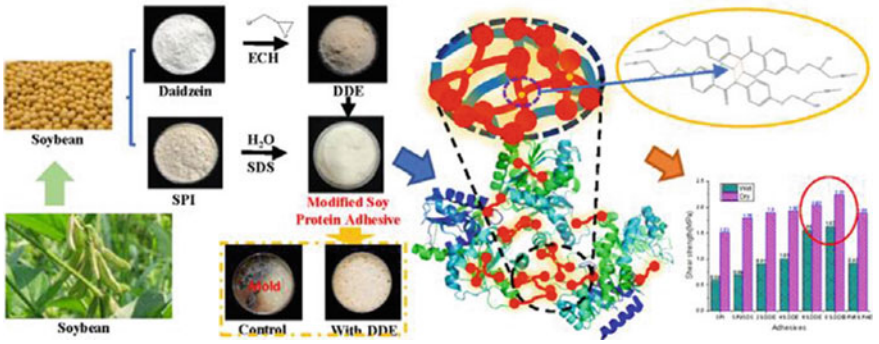

Fig. 4 Possible diagram of soy protein adhesive with high strength and mildew resistance (Xu et al. 2020)

In view of the factors of affecting the chemical modification, the reactivity of functional groups and modifier will be interesting. We mainly modified the side chain groups of soybean protein. Eslah et al. (2016) investigated the potential of chemically modified soybean flour (SF) as a strong water-resistant adhesive for plywood composites and revealed that SF with NaOH, AA, and PEI had the best adhesion performance. In addition, cross-linking agent with high reactivity was added to soybean protein adhesive (As shown in Fig. 4), and its bonding strength and water resistance were significantly improved. Soluble copper, chromium, zinc salts, aliphatic epoxides and epoxides can be used as active curing agents for basic soybean protein adhesives. Under the same technological conditions, the soybean protein adhesives obtained in the presence of epoxides have higher bonding strength. With the aim to modify soy protein-based adhesive, Pang et al. (2020) reported that a waterborne epoxy emulsion (WEU) was prepared by grafting hydrophilic groups onto bisphenol-A (E44) followed for the oil-in-water emulsion by a phase-transformation process. It is an effective way to improve the water resistance and bonding performance of soybean protein adhesives that introducing epoxy crosslinking agent. The results showed that triethylamine neutral agent could increase the wet shear strength of soybean protein adhesive by 20% compared with N, N-dimethyl ethanolamine. In comparison with pure soybean protein adhesive, the prepared adhesive reached 1.14Mpa, 192.5% higher. These properties meet the requirements for interior-use plywood ($\geq$0.7 mpa). The prepared soybean protein/WEU adhesive provides a new approach for the development of high-performance engineered wood products.

2.4 Starch-Based Adhesives

Starch molecules formed by glucose units that remove a water molecule and hold it together via glycosidic bonds. Therefore, development of starch-based adhesive with numerous the advantages such as easy workup, cost-effectiveness, non-toxic,

biodegradability and environmentally friendliness. However, because there are too many hydrophilic hydroxyl groups in the main chain of starch molecules, the adhesive strength is not ideal and it is difficult to meet the requirements of wood bonding strength. The water resistance of starch-based adhesive can be increased by chemical modification, which modification mechanism is that in the process of synthesizing starch-based adhesive, active groups such as aldehyde group, carboxyl group, amide group and isocyanate group are introduced into the liquid system of starch adhesive through oxidation, condensation, cross-linking and other reactions to change the structure of starch adhesive, so as to enhance the activity of the adhesive. After the introduction of these groups, during the curing process of the adhesive, the condensation reaction of these active groups will occur due to the change of temperature and pressure, and stable methylene bonds, urea bonds, ammonia ester bonds and other water-resistant chemical bonds will be further generated. After the cross-linking, the reticular skeleton structure will be formed, which can effectively prevent water molecules from wedging in and avoid the deterioration of adhesive performance caused by oxygen bond damage. The modified starch-based adhesive is improved by the combination of force of the newly inserted water-resistant chemical bond and a large amount of hydrogen bonds. Moreover, the structure of starch was strengthened, which improved the water resistance dramatically.

The application of starch for the development of adhesive is mainly limited to its formation naturally, which is not suitable. Therefore, it is inevitable to use various technologies and modification processes to modify starch in order to improve the performance and bonding strength of the derived adhesive. Zhou used epichlorohydrin to cross-link the oxidized starch, and then used butyl acrylate to graft copolymerize the cross-linked modified starch emulsion, to prepare the cross-linked-graft modified starch adhesive, whose properties have been greatly improved compared with the unmodified starch adhesive and with all the indicators of plywood hot-pressed dehydrated urea–formaldehyde resin, which was shown that the starch-based adhesive can adapt well to the existing production process. The most popular starch adhesive synthesis process is shown in Fig. 5. Du et al. reported that with starch as main raw material, H2O2 as oxidant, $FeSO_4$ as catalyst, borax as crosslinker, and sodium thiosulfate as stabilizer, the synthesis conditions of starch adhesive were preferred by orthogonal experiment, and then the optimal process conditions of adhesive for biochar compound fertilizer granulation were preferred. The results showed that excessive NaOH would decrease the initial viscosity of adhesive during high temperature gelatinization and in low temperature gelatinization, increasement of NaOH content can improve the initial viscosity of adhesive. At a volume of 2 or 4 mL NaOH solution was added into the oxidation stage for improving initial viscosity of prepared adhesive, thereby starch oxidation reaction was completed. When 6 mL NaOH was added in the oxidation stage, the initial viscosity of the prepared adhesive was relatively low due to excessive oxidation. The 30 wt% concentration of citric acid–starch-based adhesive with *paraserienthes falcataria* veneer was prepared by Kusumah et al. (2020) and citric acid–starch were applied in the manufacturing of plywood. The variations of compositions ratio (citric acid: starch) were 90:10, 80:20, 70:30, 60:40, 50:50 respectively. The results showed that the lamination rate

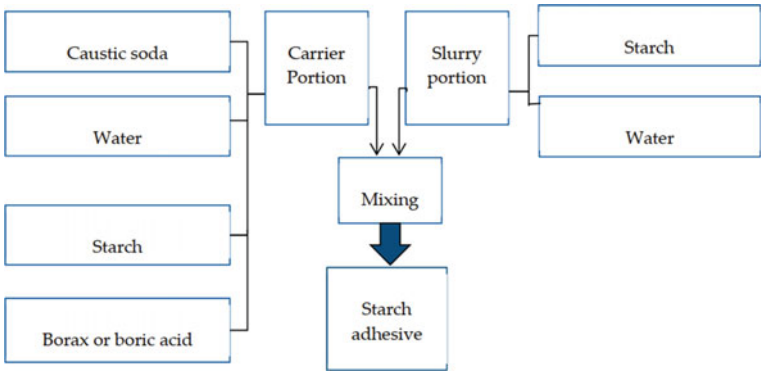

Fig. 5 The Stein Hall process (Nasiri et al. 2020)

and shear strength of plywood were the lowest when the starch content was 50 wt%. The shear strength of plywood for general utilization satisfied Standard National Indonesia (SNI).

2.5 Other Bio-Based Adhesives

The woody biomass liquefaction adhesives. Lignocellulosic biomass liquefaction refers to the thermochemical process of converting lignocellulosic biomass into liquid in the presence of some organic compounds. The liquid products of lignocellulosic biomass liquefaction in the presence of phenol can be treated as raw materials for the production of adhesives. Gao et al. prepared water-resistant wood adhesives with phenolated soy flours. Liquefaction of soybean meal in the presence of phenol degradation, not only destroyed the spherical molecules that were linked together by hydrogen bonds inside the soy protein, tightened up the spherical structure and released the spherical protein in polar group, also of the peptide chain rupture and peptides and the reaction of phenol, the activity of liquefaction reaction with formaldehyde in the flour group increase in the number, which could be used in the preparation of weather-resistant plywood. The production of adhesives by liquefaction of woody biomass has a promising prospect, but the process is not mature at present. Lignocellulosic biomass liquefaction is carried out in the presence of certain organics, which can decrease the reaction temperature to a certain extent and achieve the purpose of energy saving, but the use of liquefier increases the complexity of the process.

The pyrolytic bio-oil adhesive. The pyrolytic bio-oil adhesive uses pyrolytic bio-oil and phenol as raw materials for the synthesis of PF resin adhesives. Pyrolytic bio-oil is made from agricultural and forestry residues, which are cheap and easy to be obtained. Under the condition of isolated or limited oxygen, the organic polymer molecules in the materials can be quickly broken into short chain molecules to obtain

liquid products. The pyrolysis bio-oil of plant raw materials being rich in lignin and tannin is mainly composed of phenolic substances, which can partially replace the polymerization of phenol and formaldehyde in phenolic resin to form viscose. At present, the research on the production and applications of pyrolytic bio-oil mostly focuses on the application of pyrolytic bio-oil in energy, and the main objective of the present study is to prepare a series of adhesives for pyrolytic bio-oil.

However, the components of lignocellulosic biomass liquefaction products and the process of pyrolysis bio-oil are complex, the physical and chemical properties are relatively unstable and phase separation and precipitation may occur in long-term storage. Moreover, there are distinctive differences between the properties of different liquefaction products and pyrolytic bio-oil, so in terms of performance, the bio-oil-phenolic resin adhesive prepared by partially phenol cannot completely replace pure phenolic resin adhesive.

In addition, the phenolic hydroxyl on lignin in wood is oxidized to phenolic oxygen free radical via catalyzing of laccase, and the free radical generated is coupled to produce high polymer mass and amorphous dehydrogenation polymer. By using this reaction, the binding force of wood itself can be improved, and it is demonstrated that the use of a simple and economical approach for preparation of fiberboard and particleboard without any synthetic adhesives. The products obtained from biological engineering can be used as adhesive materials to completely get rid of the tension of chemical raw materials, which has the characteristics of self-breeding, self-fermentation, self-synthesis and self-use when manufactured.

Acetonitrile extracting lignin-based adhesive. Cui et al. (2018) reported that a lignin rigid oligomer was obtained by directly extracting lignin from pulp manufacturers with acetonitrile, which is highly polar with significantly increased carboxylic acid and reduced methoxy compared with the as-received lignin and makes the acetonitrile extracting lignin (AEL) more reactive for the preparation of adhesives. For example, Gong et al. (2020) prepared a lignin-based wood adhesive with no formaldehyde in which the AEL was used as raw material, phenolated and mixed with aqueous of polyvinylpyrrolidone. The shear strength of the adhesive could reach up to 1.70 MPa and it was still as high as 1.02 MPa after soaking for 24 h in water, meeting the National Primary Standard of plywood and according with Chinese national standard.

3 Future Challenges of Bio-Based Adhesives for Wood Composite Industries

At present, the industrial application of tannin and lignin-based adhesives is rare. Due to the high molecular weight of tannin, the prepared adhesive has high viscosity and the short application period, which limits its development and application to some extent. Lignin has also large molecular weight, complex structure, low reac-

tion activity, and requires longer hot-pressing time and higher temperature for plate making. Therefore, more lignin was used in the modification of resin and less lignin-based adhesive was prepared directly. And lignin-based adhesive also needs special processing after hot pressing. The product is black with lower physical and mechanical properties and lower water resistance. Therefore, how to reduce the molecular weight of tannin and lignin, improve the reactivity and increase the proportion of its application in viscose will be the main development trend.

Currently, soybean protein adhesives are relatively widely used in wood composite industries. Therefore, isolating soybean flour or soybean protein can be used as raw materials. The former is cheap, but the water resistance and bonding strength of the prepared adhesives are not as good as the latter. Nevertheless, the challenges such as exploring the processing technology of soybean protein separation, improving the water resistance and bonding strength of soybean protein adhesive and reducing cost, still remain, restricting its popularization application.

Starch-based adhesive has the advantages of renewable, environmental protection and low cost, but it also has disadvantages such as poor water resistance and corrosion resistance, which limits its development and application in wood composite industries. Therefore, the preparation of starch-based adhesive usually requires modification of starch first and the modified starch-based adhesive is non-toxic and environmental friendly, with good film-forming performance and adhesion performance. In addition to the mentioned above problems, the glue viscosity, low adhesive strength, short application period and dark color defects of bio-based adhesives also seriously restrict its development, becoming the main research topic in the future.

At the same time, because bio-based adhesives are bonded to other objects mainly through intermolecular forces, the strong bonding strength between wood materials and adhesives depends on many factors, including the wettability, the roughness the permeability, moisture content, the presence of wood surface extract, and the moisture absorption, the chemical composition and the pH of the wood. The bio-based raw materials can be improved by chemical methods and become wood adhesive to meet the needs of industrial production. In addition, the combination of bio-based adhesives and petrochemical adhesives, replacing some of the petrochemical adhesives, will be a good development direction. Bio-based adhesives are a kind of renewable resources with environmental protection characteristics that petrochemical adhesives cannot match, which can effectively realize sustainable development, but compared with petrochemical adhesives, corrosion resistance and drying rate need to be further improved. At present, the research and development of all kinds of biological adhesives in the world are still at the infancy stage and increasing the research intensity of biological adhesives and improving its performance are of positive significance for developing a new adhesive market and protecting the environment.

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