

Review Article

Formaldehyde Use and Alternative Biobased Binders for Particleboard Formulation: A Review

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Formaldehyde-based resins are conventionally used as a binder in formulation of particleboard. Epidemiologic studies have shown that formaldehyde is carcinogenic. Efforts to reduce the health hazard effects of the formaldehyde-based resin in the particleboard formulation have included use of scavengers for formaldehydes and use of an alternative binder. Use of scavengers for the formaldehyde increases the cost and maintenance of particleboard formulation. There is no proof that scavengers eliminate the emission of formaldehyde from particleboard. Use of biobased binders in particleboard formulation provides an alternative for eliminating use of the formaldehyde-based resin. However, the alternative is hindered by challenges, which include limitations of physical and mechanical properties. The challenge has continuously been acted upon through research. The paper presents an overview of the use of starch as an alternative binder. Improvement over time of the starch and limitations thereof requires to be addressed. Use of the modified starch has shown increased particleboard performance. Mechanical strength, such as modulus of rupture, modulus of elasticity, and internal bonding in particleboards, however, remains to be a challenge.

1. Introduction

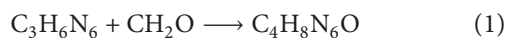
1.1. Formaldehyde-Based Resins and Particleboard Formulation. Formaldehyde is used in industries for the synthesis of resins and adhesives used during formulation of particleboard [1]. Phenol formaldehyde (PF) resins are used as adhesive for fixing together panels of exterior-grade plywood, the flakes of oriented strandboard panels, and particleboard [2]. Phenol formaldehyde resins provide high standards of physical and mechanical properties, which involve high strength and resistant to moisture. This prevents delamination and gives excellent temperature stability. This is due to the more flexible nature of phenolic resins [3]. However, high cost of PF is due to fluctuations in cost of phenols and undergoes hydrolysis to emit formaldehydes. Investigation aimed at use of cheaper and formaldehyde-free products as substitute of phenol-formaldehyde, based on not only environmental but also economic grounds. Lignin has comparatively low price and high phenolic moieties along

with environmental considerations render it as a suitable substitute for phenols in the manufacture of PF [4, 5].

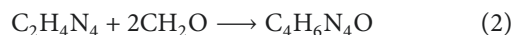
Urea formaldehyde (UF) resin is widely used as adhesives in the particleboard industry. UF is cheaper compared to PF. There are two major limitations of wood composite boards based on UF binders: first, high emission of formaldehyde during both production, and second, subsequent exploitation of the boards [6]. Particleboard formulated with urea formaldehyde shown pronounced thickness swelling to water, and hence, they are unsuitable for outdoor use [7]. Measures used to reduce formaldehyde emissions involve decrease of the formaldehyde/urea molar ratio [8]. Unfortunately, the decrease in formaldehyde/urea ratio has resulted in deterioration of physical and mechanical properties of particleboard at the same time.

1.2. Formaldehyde Emission and Formaldehyde Scavengers. The other method used to reduce formaldehyde emission is by use of chemical additives called formaldehyde scavengers.

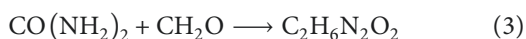
The most commonly used scavengers are compounds containing amine such as urea, ammonia, melamine, and dicyandiamide [9]. Melamine reacts with formaldehyde to form methylolamine as shown in equation (1) [10]:



Dicyandiamide reacts with two moles of formaldehyde as illustrated in equation (2) to form methyloldicyanamides [11]:



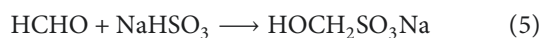
Urea reacts with formaldehyde to form mono-methylolurea as shown in equation (3) [12, 13]. Urea formaldehyde resin is used in formulation of particleboard as a binder, other than a scavenger.



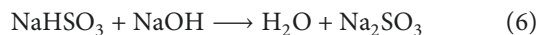
Sodium metabisulphite ($\text{Na}_2\text{S}_2\text{O}_5$) is a scavenger used in particleboards produced with urea formaldehyde and melamine formaldehyde resins. Sodium metabisulphite reacts with water to form sodium hydrogen sulfite, as shown in equation (4).



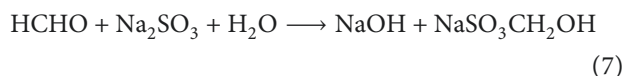
Sodium metabisulphite reacts with formaldehyde as a scavenger to form a bisulfite adduct [14] as shown in equation (5):



Sodium hydrogen sulfite also reacts with sodium hydroxide to form sodium sulfite, as shown in equation (6):



Sodium sulfite scavenger formaldehyde in the presence of water to form bisulfite adduct, as in equation (7) [14].



Ammonia is a good scavenger for the emitted formaldehyde [15]. Green tea catechin as a formaldehyde scavenger reduced formaldehyde from plywood manufactured with formaldehyde-based resin. Green tea extract reduced formaldehyde emissions from plywood [16]. Proanthocyanidic was found to protect kidney tissue against formaldehyde [17]. Tannin was mixed with low molecular phenol-formaldehyde resin in manufacture of plywood. It was used to scavenge against emitted formaldehyde [18].

Prolonged human exposure of formaldehyde lead to chronic toxicity and cancer [12, 19]. Formaldehyde can cause nasopharyngeal cancer [20]. Lu et al. [21] reported on genotoxic and cytotoxic modes of action for the carcinogenesis of inhaled formaldehyde in respiratory nasal epithelium [21]. An increased incidence of myeloid leukemia has been reported.

Increased exposure of formaldehyde to workers in a funeral homes resulted in mortality from myeloid leukemia [22] and lymphohematopoietic malignancies [23–25]. The most consistent pattern was death as a result of myeloid leukemias

[26]. A study of 11,039 textile workers produced a certain relationship between the duration of formaldehyde exposure and leukemia-related deaths [27]. The exposure assessment based on 594 workers produced the mean exposure levels between 0.09 and 0.20 ppm, and the levels were relatively constant with no peaks or intermittent exposures. Leukemia had the highest standardized mortality ratio (SMR) with majority of occurrences from garment factory. The epidemiological literature on formaldehyde and leukemia is extensive. Many studies have shown a correlation between formaldehyde and cancer-related complications [26].

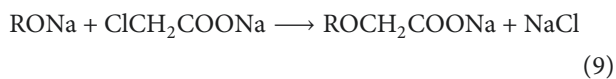
1.3. Use of Starch and Starch Derivatives as Substitutes for Particleboard Formulation. Adhesive technology is moving towards replacements of formaldehyde-based adhesives to use of biobased resources [28–30]. Various types of starch modification on its crystalline nature include chemical treatments such as oxidation using hypochlorite [31] and air [32], esterification [33], and cationization [34, 35]. Physical modification of starch includes mechanical activation [36], microwave [37, 38], ultrasonic degradation [39, 40], heat-moisture treatment [41], and enzymatic treatment [42–44]. The modified starch has been utilized in particleboard formulation [45–48].

Selamat et al. [46] compared physical and mechanical properties of particleboard formulated from rubberwood with urea formaldehydes and native starch, separately as binders. The native starch was extracted from oil palm trunk. Particleboard bonded with formaldehyde showed thickness swelling of 11.17% and water absorption of 82.08%, when compared to the native starch with thickness swelling of 82.08% and water absorption of 174.52% [46]. This shows that formaldehyde-based resin is more than twice better than the carboxymethyl starch, although the main drawback is emission of formaldehyde. Formaldehyde has been found to have carcinogenic properties [21, 49–51]. High water absorption of particleboard formulated with the carboxymethyl starch may be attributed to the presence of hydroxyl groups. Hydroxyl groups form hydrogen bonding with water. This increases water absorption and thickness swelling, thus affecting mechanical properties of the particleboards. Methylene diphenyl diisocyanate (MDI) were small and had better mechanical and chemical bonding ability [52]. Improvement in chemical bonding results in improvement in mechanical properties of the particleboard formulated.

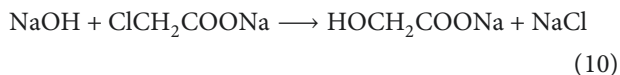
Natural starch is in the disorganized metastable state and as such is easily dispersed in warm water [53]. Carboxymethylation therefore is a chemical modification method that is vital and versatile for transforming starch. Transformation of starch involves provision of water soluble polymers and intermediate of valuable functional attributes [54]. Carboxymethylation of starch (CMS) involves partial substitution of hydroxyl group (-OH) with ether group (-O-CH₂COOH). Starch reacts with monochloroacetic acid to produce carboxymethyl in the presence of sodium hydroxide in three different steps. Step one involves reaction of starch with starch, as shown in equation (8):



Step two involves the reaction between sodium salt formed with monochloroacetic acid to form sodium monochloroacetate (SMCA) as shown in equation (9):



Alternatively, SMCA reacts with sodium hydroxide to form sodium glycolate:



Carboxymethylation therefore improves the rheological property of the native starch that improves particleboard characteristics [54].

Starch in water undergoes limited reversible swelling, but the integrity of the crystal structure is such that it does not dissolve [55]. Starch gelatinization at low temperatures can be induced by addition of aqueous alkali [56]. Sodium hydroxide reacts with hydroxyl groups of starch thus improving the thickness swelling and water absorption of the native starch by 8% and 22%, respectively. This is attributed to reduction of hydroxyl groups that were reacted with sodium hydroxide. Another reason could be as a result of reaction between carboxylic group in monochloroacetic acid and hydroxyl groups in starch through esterification process. Particleboard bound with urea formaldehyde had the highest modulus of rupture (MOR) values for medium density of 9.63 N/mm², while those bound by the native starch gave the lowest of 3.38 N/mm². Same trend was found in modulus of elasticity and internal bonding with 3369.12 N/mm², 2068.95 N/mm² and 1.98 N/mm², 0.96 N/mm², respectively [46]. Improved mechanical strength from the native starch to carboxymethyl starch is attributed to the cross-linking of the composite material with highly branched carboxymethyl, leading to formation of stronger covalent bonds than hydrogen bonding found in the native starch. Carboxymethyl starch treatment improved the MOR, thus attaining the minimum Japanese Industrial Standard [46]. MOR is still very low compared to particleboard formulated from urea formaldehyde. There is no interaction between the functional groups of the lignocellulose material and the starch, which leaves a major deficit in reinforcement of the bond between the components of the particleboard. This presents a challenge that requires consideration. Treatment with sodium hydroxide and temperature reduces the sizes of starch making them disperse more within the lignocellulose matrix.

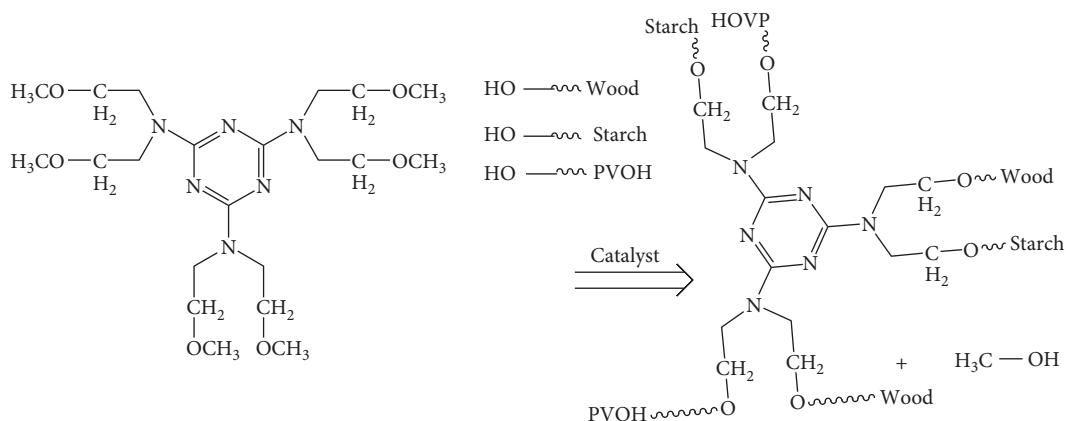
Despite the growing interest in bioplastics, the use of starch-based plastic is still limited due to its brittleness and moisture sensitivity. Addition of polyvinyl alcohol (PVA) reduces the brittleness of the bioplastic [57], and latex increases water resistance [58]. Shi and Tang [47] used polyvinyl alcohol solution with styrene-butadiene (SBR) latex and polymeric methyl diphenyl diisocyanate to modify corn starch. Particleboard formulated showed MOR range from 13.26 N/mm² to 16.54 N/mm², MOE range from 1508 N/mm² to 1768 N/mm², and IB range from 0.17 N/mm² to 0.32 N/mm² [47]. Starch-based adhesives gave the

particleboard better prepressing property and sizing uniformity. Pan et al. [59] used polymeric methylene diphenyl diisocyanate to modify rice bran for making an adhesive for making particleboard. Average MOE for particleboard formulated was 2545 N/mm², MOR, 21 N/mm², and IB of 0.35 N/mm² [59]. The study showed that the rice bran adhesive produced can be used to replace a portion of the synthetic adhesive pMDI currently used for the fabrication of rice straw particleboard. Addition of PVA, latex, and SBR will improve moisture resistance, water absorption, and thickness swelling which in turn reduces mechanical properties.

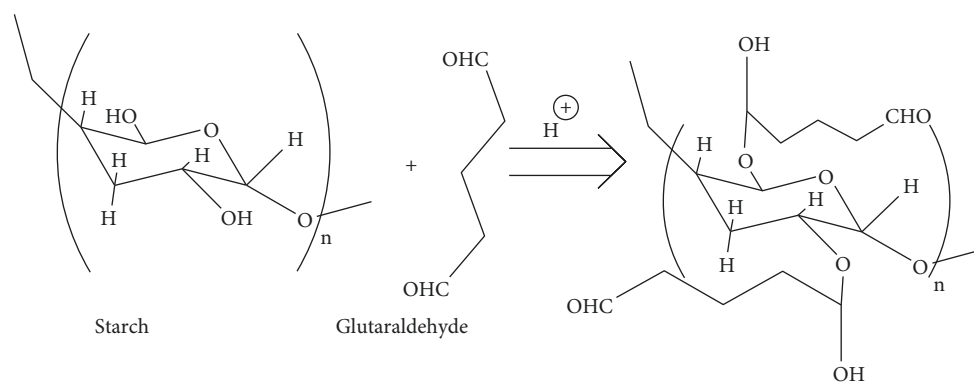
Xu et al. [60] used butyl acrylate (BA) as a comonomer in synthesizing the corn starch-based wood adhesive. The bonding performance was close to that of commercial polyvinyl alcohol solution. This cassava-based wood adhesive (SWA) improved in stability more than the corn starch-based wood adhesive. Improved stability was attributed by its low minimum film forming temperature (MFFT) and glass transition temperature (*T_g*) of the cassava starch [60]. Zhu and Zhuo [61] used butyl acrylate to modify the corn starch used for encapsulating carboxylic-containing compounds through graft copolymerization. The encapsulated organic materials showed low swellability, large encapsulating capacity, and low solubility in water [61]. Low swellability property is crucial in formulation of particleboards. Liu and Su [62] used butyl acrylate to modify potato starch through grafting via surface-initiated atom transfer radical polymerization [62]. Graft modification provides a significant route to alter physical and mechanical properties of biobased adhesives [63].

Starch contains many hydroxyl groups, which make it extremely polar leading to low interaction with nonpolar materials [64]. Starch-based adhesives wet the polar surfaces of cellulose, penetrate crevices and pores, and, thus, form strong bonds. Imam et al. [65] cross-linked corn starch with polyvinyl alcohol (PVOH) using hexamethoxy methylmelamine (HMMM) to bond lignocellulose materials together in an acidic medium. Under this condition, methoxy groups from HMMM reacted with the hydroxyl group from starch in the presence of PVOH to form ether bond [65], as in Scheme 1.

Ether bonds are covalent bonds which are stronger than hydrogen bonding in starch. The binder in formulated particleboard remained intact showing superior bond strength establishment. The boards fractured during mechanical testing. This is attributed to use of an acid media during particleboard formulation. The use of an acid media limits activation of functional groups in lignocellulose materials. Particleboard made from rice straw and the polyvinyl starch-based adhesive gave the following results: MOR, IB, and TS of up to 31 N/mm², 0.49 N/mm², and 20%, respectively [65]. Use of urea formaldehyde-based resin as a binder gave MOE, IB, and TS of up to 22.19 N/mm², 0.5 N/mm², and 75% [66]. Researchers worked with different particle sizes and found that the starch-based adhesive gave comparatively better physical and mechanical properties. Properties of polyvinyl alcohol-based resin were greatly influenced by the interaction between the adhesive and



SCHEME 1: Schematic chemical crosslinking reaction [65].

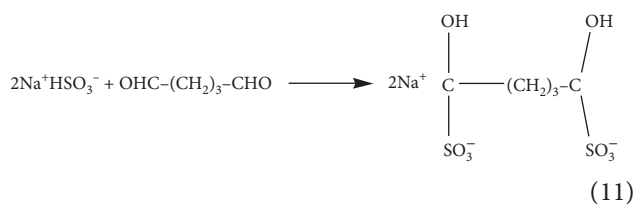


SCHEME 2: Modified starch by glutaraldehyde.

lignocellulose material. These properties are still below expectations and can be boosted by use of an alkali, which activates functional groups in lignocellulose materials [67].

Akinyemi et al. [68] used glutaraldehyde to degrade the cassava starch in the presence of acidic medium. Hydroxyl groups in starch molecules were replaced by glutaraldehyde as indicated in Scheme 2.

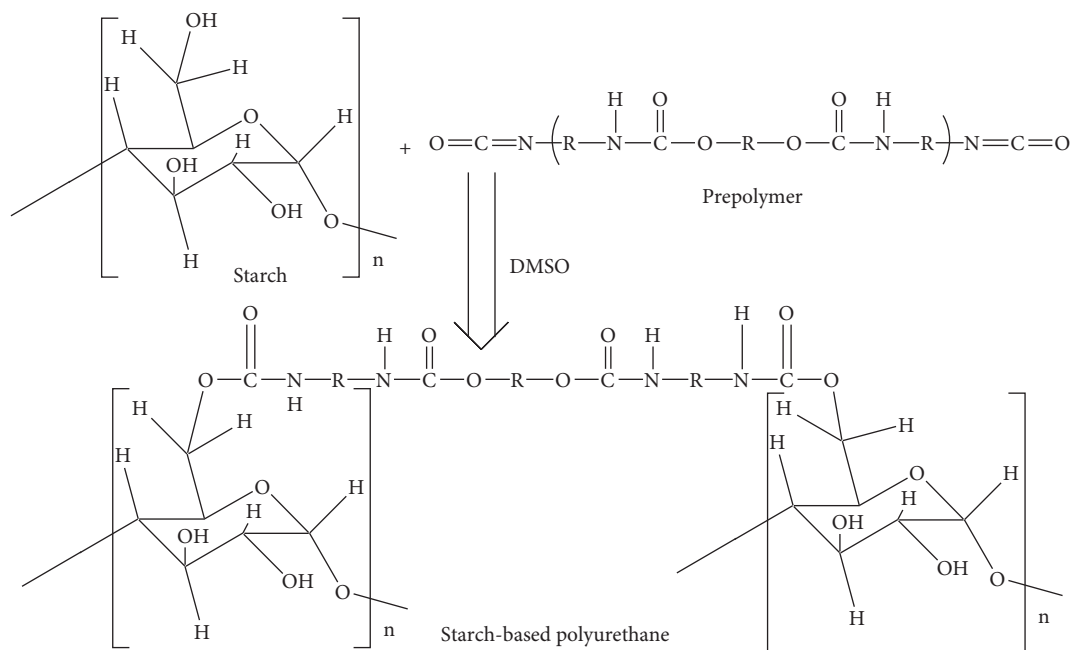
The modified starch was used to bind wood chips in formulation of sawdust particleboard. Particleboard formulated using this modified starch gave the following results: MOE and MOR of 3232 N/mm², and 35.7 N/mm², respectively. Comparatively, melamine-formaldehyde (MF), was also used by Cui et al. [69] to obtain MOE and MOR of 2701 N/mm² and 14.21 N/mm², respectively [68]. MF undergoes hydrolysis leading to produce formaldehyde. Starch modified with glutaraldehyde gave better mechanical strength than their formaldehyde counterpart. Glutaraldehyde is harmful, and this has necessitated the use of sodium bisulfate as a scavenger to neutralize its effect [70]:



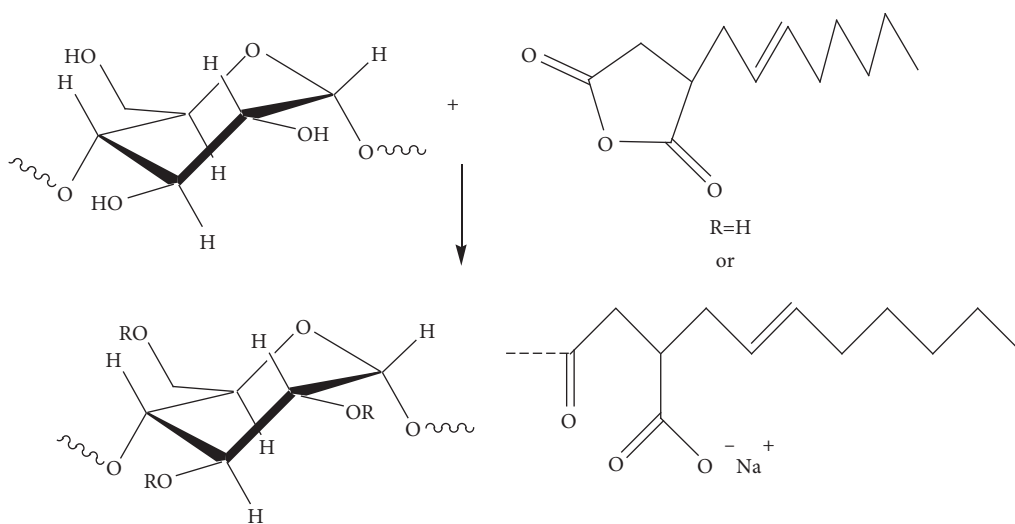
Starch reacts with polyurethane polymer via terminal hydroxyl group in starch through grafting [71], as shown in Scheme 3.

Polar hydroxyl groups are replaced with the hydrophobic aromatic urethane functional group [72]. Polyurethane has been used to modify castor oil starch used in formulation of particleboard made from sugarcane bagasse. The board had WA, TS, MOE, MOR, and IB of up to 20.1%, 20%, 22.6 N/mm², 2850 N/mm², and 1.18 N/mm², respectively [73]. Urea formaldehyde and melamine formaldehyde resin binders for sugarcane bagasse produced WA, TS, MOR, MOE, and IB of 64.87% and 32.52%, 24.71% and 12.66%, 757.8 N/mm² and 1053.28 N/mm², 3.66 N/mm² and 5.53 N/mm², and 0.2 N/mm² and 0.45 N/mm², respectively [74]. Formaldehyde-based resin produces formaldehyde which is a carcinogen. Although modified starch resin produced higher physical and mechanical properties compared to its formaldehyde-based resin, its properties are still very low. Mechanical properties of particleboard made using starch-based adhesive modified polyurethane improved by crosslinking with lignocellulose material.

Starches modified with octenyl succinic anhydride (OSA) have been used in a range of industrial applications, particularly as a food additive. OSA is hydrophobic and also has steric effects. Starch reacts with OSA to form starch octenyl succinate as shown in Scheme 4.



SCHEME 3: Preparation of starch-based polyurethane [70].



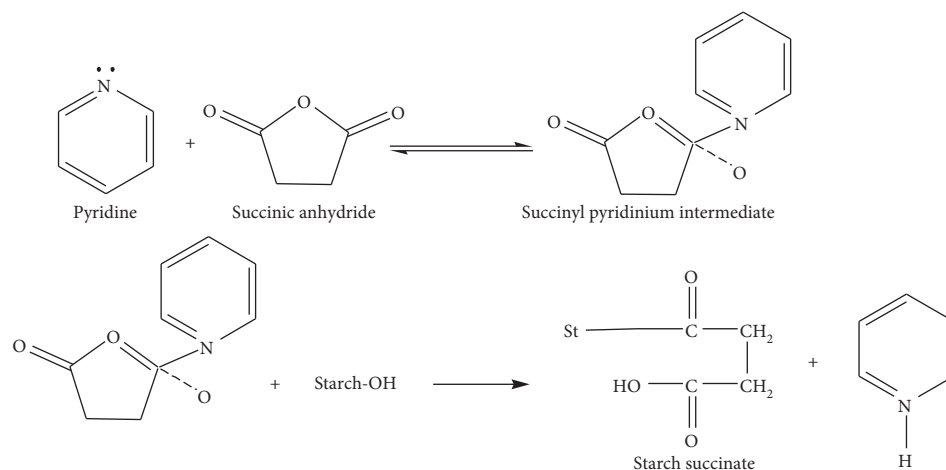
SCHEME 4: Reaction showing starch modified with octenyl succinic anhydride (OSA).

Sweedman et al. [75] modified *indica* rice, maize, waxy maize, and potato with octenyl succinic anhydride (OSA) between the temperatures of 30 to 40°C. Due to hydrophobic and steric contributions of OSA and highly branched macromolecular starch structure, modified starch display useful stabilizing, encapsulating, interfacial, thermal, nutritional, and rheological properties [75]. Altuna et al. [76] modified starch with octenyl succinic anhydride to yield a hydrocolloid with amphiphilic properties, the octenyl succinylated starch. The octenyl succinylated starch finds wide application in the food industry mainly as emulsifier, encapsulating agent, and fat replacer [76]. Research investigating the reaction between OSA and modified waxy maize starch showed that OSA reacts with maltodextrine

better than the native starch. This indicates incorporation of OSA into hydrated granules [77].

Succinic anhydride reacts with starch by refluxing with pyridine or by gelatinization of starch in aqueous pyridine. This is followed by a reaction with succinic anhydride in pyridine. Pyridine has a dual function in the reaction, activates starch, which makes it nucleophilic, and reacts with succinic anhydride to form succinyl pyridinium intermediate. The intermediate reacts with starch generating starch succinate and pyridine as shown in Scheme 5 [78].

Mehboob et al. [79] used succinic anhydride to modify the native sorghum starch and acid-thinned starch. Succinylation of starch introduces succinyl groups that have hydrophilic character to starch [79]. This group weakens



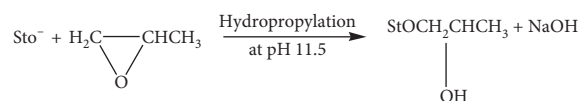
SCHEME 5: Starch modification with succinate and pyridine.

internal bonding in starch granules and leads to solubilization of starch in cold water. Research has shown that succinylation reduced retrogradation in starches while the peak, cold paste and water-binding capacity, and set back viscosities improved [77]. Olayinka et al. [80] demonstrated that these parameters are increased by succinylation of red sorghum starch and decreased by modification of a white sorghum starch. The researcher stated that starch succinates have advantages such as high viscosity, greater thickening power and low gelatinization, and retrogradation [80]. Succinylated starches are used in preparation of nongelling creams due to the increase in viscosity of starch. Its improved hydrophilicity [79] makes them suitable for use as a binder in particleboards.

Hydroxypropylation is a common etherification method for starch through treatment with propylene oxide in an alkaline media [81]. Starch reacts with propylene oxide to form the hydroxypropyl starch as shown in Scheme 6.

Hydroxypropylation decreases the ability of starch to recrystallize, which reduces the retrogradation property of starch, yielding a derivative that is stable at high temperatures [82]. Hydroxyl groups are substituted with hydroxypropyl groups making its physicochemical properties similar to those of the carboxymethylation method. Hydroxypropyl groups disrupt inter- and intramolecular forces in starch, thus breaking hydrogen bond. This weakens the starch granules leading to its flexibility of amorphous region. Water uptake increases and thus an increase in the swellability [83]. Hydroxypropylation increases starch solubility in water and has stabilized solubility [84]. Hydroxypropylation reduces the number of hydroxyl groups in starch. This in turn reduces the hydrophilic properties of particleboards formulated with the hydropropylated starch. This will reduce water absorption and thickness swelling of the particleboard.

Native starches are present in semicrystalline granular forms with certain thermal properties and functionality that have permitted its industrial use. Starch requires high heat to undergo a transition process, during which the granules break down into a mixture of polymers-in-solution, known as gelatinization. Sodium hydroxide solution reduces the temperature required by the starch to gelatinize [85].



SCHEME 6: Hydroxypropylation of starch with propylene oxide.

Sodium hydroxide is meant to stabilize the viscosity of starch adhesives when they are subjected to high shearing action, heat for prolonged periods, or freeze-thaw cycles [86]. Starch reacts with sodium hydroxide to produce a cationated starch as shown in Scheme 7.

Other plasticizers apart from water and aqueous alkaline, include salt solution such as calcium chloride and potassium iodide [87]. Starch, a polyol, reacts with borax to form a borax-starch complex [88] as illustrated in Scheme 8.

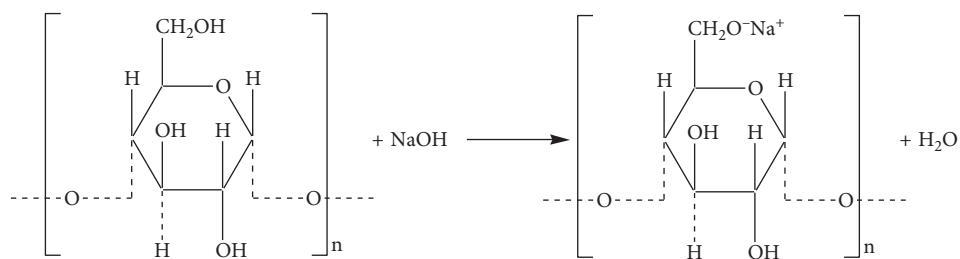
Sodium hydroxide delignifies lignocellulose material by cleavage of the β -O-4 ether bond in which sodium cation and hydroxide ion participate [89], as illustrated in Scheme 9.

Activated starch reacts with lignin in lignocellulose material to form a plasticized starch blend [90] as shown in Figure 1.

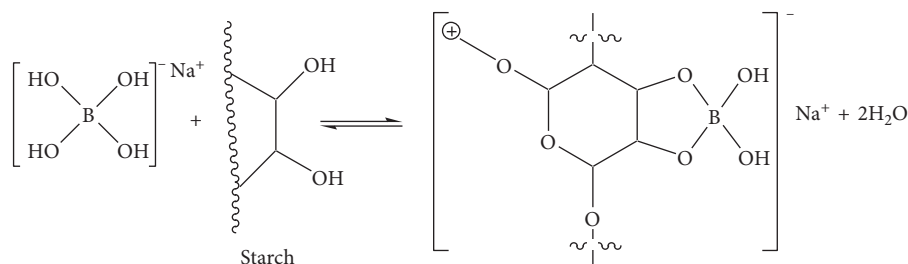
Delignification takes place during cellulosic ethanol production to form free cellulose, hemicellulose, and lignin [91]. High concentration of sodium hydroxide converts cellulose and hemicellulose into organic acids, furfural, and hydroxymethyl furfural [92]. An organic acid such as lactic acid has been used in crosslinking of starch and furfural. Furfurals were used as a substitute of formaldehyde in particleboard formulation, respectively. Lignin hydroxyl groups are oxidized to carboxylic acid in the presence of sodium hydroxide as a catalyst [93]. Carboxylic acid reacts with starch hydroxyl groups to form an ester. Ester formation is the main linkage point between the lignocellulose materials and starch binders in the proposed composite formulation for particleboard.

Citric acid and sucrose are natural adhesives [45]. Citric acid is an organic polycarboxylic acid, which contains three carboxyl groups used as cross-linking agent for wood, through esterification [94], as shown in Figure 2.

Liao et al. [45] bonded sugarcane bagasse with commercial sucrose-based adhesive modified with citric acid in the production of particleboard. The board produced had a



SCHEME 7: Reaction between starch and sodium hydroxide.



SCHEME 8: Starch molecules crosslinked with borax.

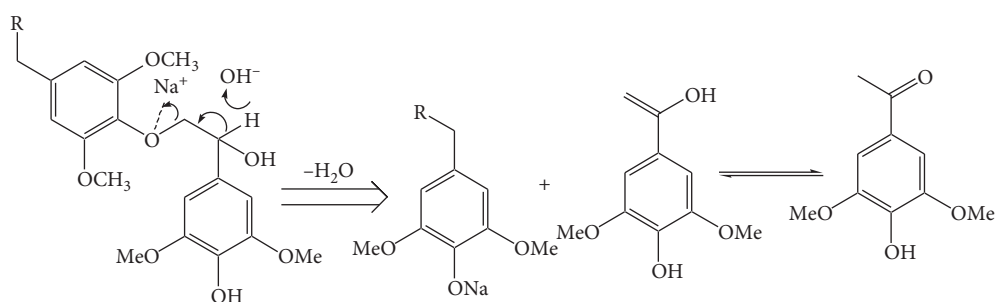
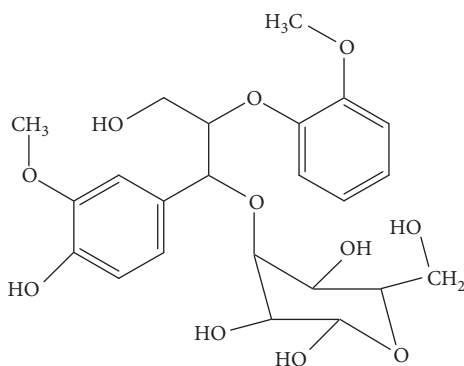
SCHEME 9: Cleavage of the β -O-4 bond and formation of syringyl derivatives.

FIGURE 1: Ether bond formed between starch and lignocellulose material.

density of 0.45 g/cm^3 , a low density particleboard [45]. Board density between 0.35 and 0.45 g/cm^3 produced modulus of rupture (MOR) of 6.2 N/mm^2 [45]. The particleboard showed good thermal insulation properties when used as building material for thermal insulation applications. Particleboards produced had a density of 0.40 g/cm^3 met the

requirement of Chinese national forestry industry standard. Sugarcane bagasse is rich in sugar-containing compounds that make it suitable for particleboards manufacturing [45].

Starch hydrolyzed with acid followed with oxidation lead to the formation of aldehyde starch [95] as shown in Scheme 10.

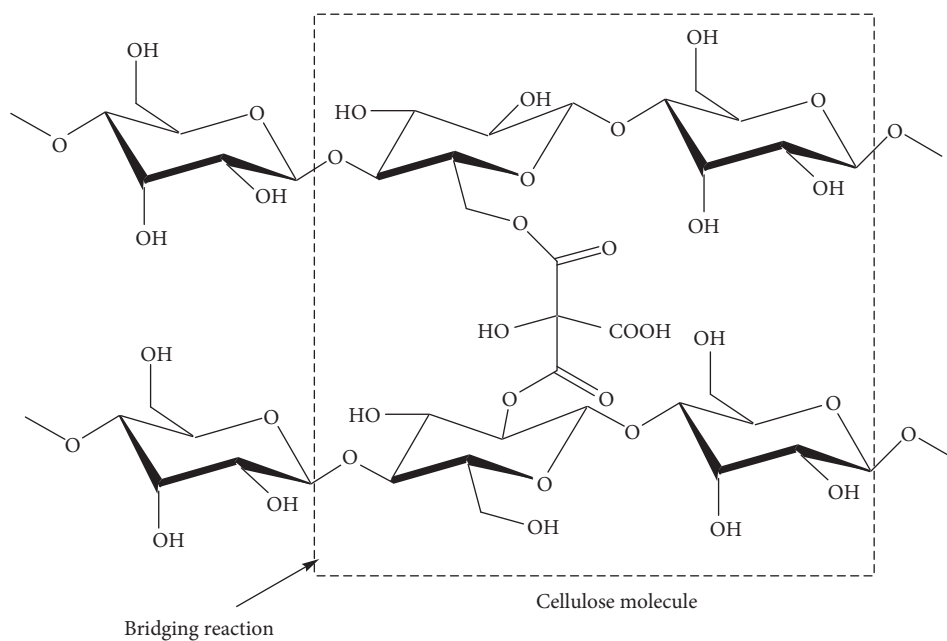
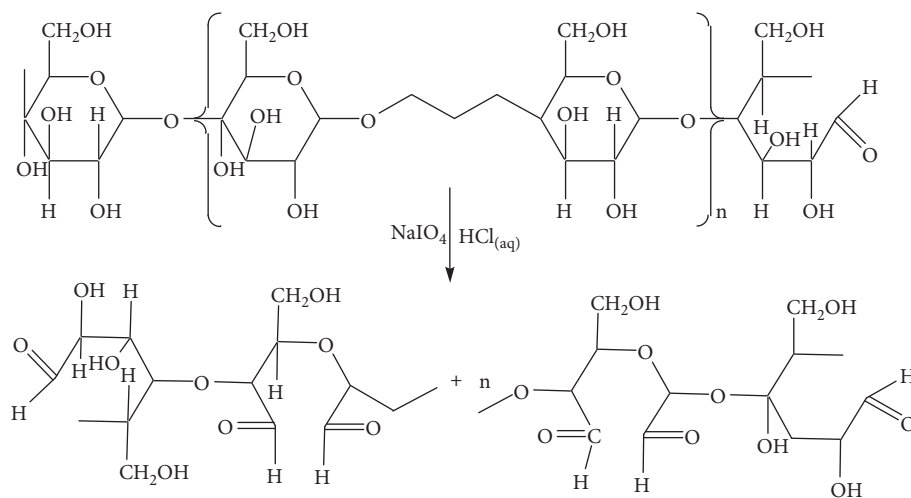


FIGURE 2: Reaction between citric acid and cellulose molecules [45].



SCHEME 10: Reaction of acid hydrolysis and oxidation of starch.

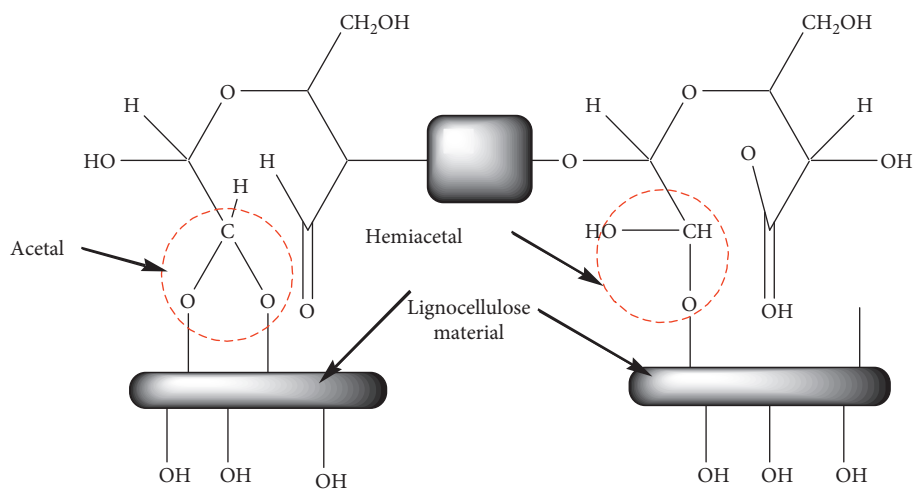


FIGURE 3: Acetal and hemiacetal bondages between lignocellulose material and modified starch.

Starch dialdehyde reacts with lignocellulose material to form acetal and hemiacetal bondage [96, 97] as proposed in Figure 3.

2. Conclusion

Starch structural and functional diversity make it suitable for different applications. Various modifications will change and improve functional properties of starch and facilitate its utilization for different purposes. Starch modified with other chemicals is used as a substitute for formaldehyde-based resin in particleboard formulations. Hydroxyl group modification in starch is achieved through the introduction of alkyl groups or oxidation to carboxylic acid. This reduces the hydroxyl functional groups that determine the water absorption and thickness swelling which in turn affect the mechanical properties of particleboard. Functional groups in lignocellulose materials determine the water and thickness swelling. Interaction between modified starch-based resin and lignocellulose materials improve properties of particleboard. Mechanical strength of particleboard made from starch-based resin is due to reaction between starch and lignocellulose materials. The hydroxyl group in starch and carboxylic group in lignocellulose materials react through condensation polymerization to form ester linkages. Esterification produces hydrophobic material that reduces water absorption. Esterification also results in formation of covalent bonding that increases the interaction between components of particleboards. This in turn increases the mechanical properties of the particleboard. Unmodified hydroxyl groups in both starch and lignocellulose materials undergo etherification forming a covalent bond through ether bond. Ether and ester linkages are covalent bonds, stronger than hydrogen bonding found between the untreated starch and lignocellulose materials. Physical and mechanical properties of particleboards produced from starch-based adhesives are improved by crosslinking of the starch and lignocellulose material using borax.

Disclosure

This review is part of Ph.D. research project without any research funds.

Conflicts of Interest

The authors declare no conflicts of interest.

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