

Starch-Based Adhesives for Wood/Wood Composite Bonding: Review

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Abstract

Increasing global energy crisis and scarcity of petroleum resources has shifted focus of chemical industries to look for alternative raw material resources. The main focus of raw materials in wood adhesives, such as petroleum and natural gas [1] [2], would be gradually replaced by renewable biopolymers. Starch is a relatively inexpensive and renewable product from abundant plants, easy processing and it has been extensively used as binders, sizing materials, glues and pastes [3], but its bonding capacity is not strong enough to glue wood [4]. Extensive research has been carried out on improving the cohesive properties, especially water resistance, of starch-based adhesives. In starch-based wood adhesive many new approaches have come forward for effective use it in wood/wood composite adhesive giving comparable performance as synthetic adhesives. This review of starch-based adhesives is made with the focus on starch modification methods for improving properties of starch-based adhesives.

Keywords

Bio-Polymer, Starch, Wood Adhesives, Cross-Linking, Composite

1. History of Wood Adhesive

As early humans moved from a nomadic to the settled existence, they needed structures and furniture in those structures that were more permanent. Many of these were made using mechanical connectors, but humans were also looking for adhesives from plants and animals. Some, such as blood, pitch, gums, and rubber latexes, could be used as adhesives and sealants with no processing. Others, such as casein from milk, soybean proteins, and collagen adhesives, needed more processing. Animal glues from collagen, blood glues, and casein glues from milk have been used for a very long time; fish glues originated in the 1800s and soy glues in the 1900s. The first wood glues needed limited strength because they

were used for interior applications, such as furniture. The desire to use wood more efficiently was an impetus for adhesive development in the 19th and 20th centuries. Two major early developments were the use of casein for glulam production and soy adhesives for interior plywood. Despite some success with bio-based adhesives, they were replaced by synthetic adhesives starting in the 1930s, mainly due to economics, water resistance, and ease of use. Tannins have been used for many years as a wood adhesive in locations where they are readily available and where phenolics are more limited in supply and are more costly. Carbohydrates are not used in wood bonding because of their water and thermal sensitivity. Synthetic adhesives Phenol-formaldehyde as one of the original synthetic polymers, and its application to wood bonding in the 1930s allowed for the development of durable exterior plywood. PF allowed for the development of exterior plywood, and the similar resorcinol-formaldehyde and phenol-resorcinol-formaldehyde allowed for the development of more durable glulam and other structural wood products. Urea-formaldehyde, being a low-cost, effective adhesive, has led to the expansion of existing interior products and the development of new panel products. Melamine-formaldehyde adhesives, being more water resistant but more expensive than urea-formaldehyde, has been used to improve urea-formaldehyde adhesives or used by itself as an exterior adhesive, especially outside North America. After World War II was a prime period for the development and growth of many other synthetic polymers. Some found use as very successful wood adhesives. The main ones were poly (vinyl acetate), isocyanates, and polyurethane. Others were aliphatic resins, epoxies, and construction adhesives. A main advantage of these adhesives has been that they can be formulated to have a wide range of properties, depending on the types and ratio of monomers. An important advantage of synthetics over natural products has been the ability to formulate the polymer backbone rather than trying to use what nature has provided [5]. Though synthetic adhesives have advantage in performance parameter, they have drawbacks like high formaldehyde emission, finding alternate resources for raw material is the only solution for increasing scarcity of petroleum resources, the mainly used raw materials of wood adhesives is being replaced by renewable biopolymers, such as soybean protein [6] [7] [8], natural tannin [9] [10] [11] and starch [12]. Starch is a kind of renewable, biodegradable, inexpensive, and readily available biopolymer extensively used as binders, glues, and pastes [13]-[20]. In all biopolymers stated above starch is easily available and low cost, many studies have been carried out which has given comparable results.

2. Starch Composition and Its Structure

Starch is an abundant, inexpensive, renewable and biodegradable polymer. It is the second most abundant natural polymer after cellulose and can be obtained mainly from the roots, stalks and seed of staple crops such as rice, corn, wheat, tapioca and potato.

Starch structure:

Starch is a polysaccharide, basically polymers of the six-carbon sugar D-glucose, often referred to as the “building block” of starch. The structure of the monosaccharide D-glucose can be depicted in either an open-chain or a ring form (Figure 1).

Starch consisting of D-glucose units, referred to as homoglucon or glucopyranose, and two major bio-macromolecules-amylose and amylopectin.

Starch composition: Amylose and amylopectin in starch

Amylose:

Amylose is a relatively long, linear polymer composed almost entirely of α -1,4-linked D glucopyranose (Figure 2). Amylose has a molecular weight of approximately $1 \times 10^5 - 1 \times 10^6$ and a degree of polymerization (DP) by number (DPn) of 324 - 4920, with around 9 - 20 branch points equivalent to 3 - 11 chains

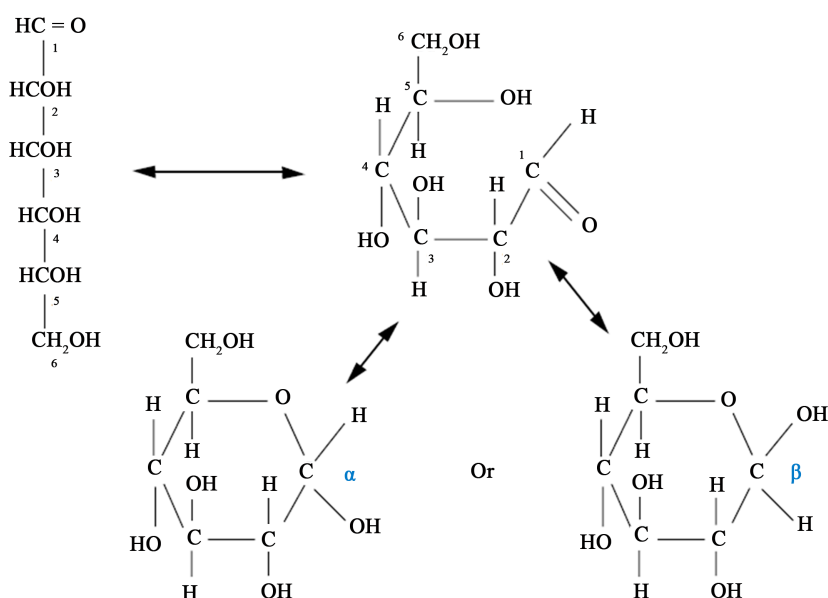


Figure 1. Open-chain and pyranose ring structures of the hexose sugar D-glucose [21].

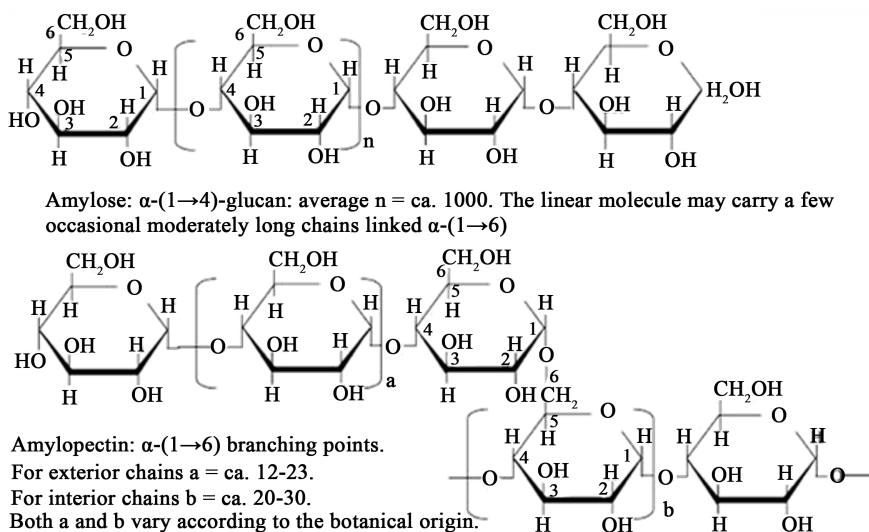


Figure 2. Structure of amylose and amylopectin. Adapted from Tester & Karkalas (2002).

per molecules [22]-[28]. Another well-known attribute of amylose is its ability to form a gel after the starch granule has been cooked, *i.e.*, gelatinized and pasted. This property is evident in the behavior of certain amylose-containing starches. Corn starch, wheat starch, rice starch, and particularly high amylose corn starch isolated from hybrid corn plants are usually considered gelling starches. Gel formation is primarily the result of the re-association (*i.e.*, retrogradation) of solubilized starch polymers after cooking and can occur quite rapidly with the linear polymer amylose [29] [30] [31] [32] [33].

Amylopectin:

The literature proposes several models for helical configurations, branch chains, cluster patterns, and molecular dimensions of amylopectin. Amylopectin, the predominant molecule in most normal starches, is a branched polymer that is much larger than amylose. Amylopectin is composed of α -1,4-linked glucose segments connected by α -1,6-linked branch points [34]-[40]. The small chains have an average degree of polymerization (DP) of about 15, whereas that of the larger chains is about 45.

Other constituents of the starch granule:

Proteins, lipids, moisture, and ash (minerals and salts) are also present in starch granules in very small quantities [41] [42] [43] [44].

Different types of starch and their composition

Amylose to amylopectin ratio within a given type of starch is a very important point to consider with respect to starch functionality as adhesives. Content of amylose and amylopectin in various starches are shown in **Table 1**.

3. Starch: Used as Wood/Wood Composite Adhesive

3.1. To Reduce % Formaldehyde Released in UF Resin Adhesive for Wood Composite

Urea formaldehyde resins are preferred for bonding plywood and other wood based panels mainly due to the easy availability of raw materials required for resins at lower costs, colorless glue line and fast setting at elevated temperatures [45].

Disadvantages of UF resin:

Table 1. Approximate amylose and amylopectin content of common starches.

Starch Type	Amylose Content (%)	Amylopectin Content (%)
Dent corn	25	75
Waxy corn	<1	>99
Tapioca	17	83
Potato	20	80
High-amylose corn	55 - 70 (or higher)	45 - 30 (or lower)
Wheat	25	75
Rice	19	81

- Upon addition of water, in high temperature, cured urea formaldehyde can hydrolyze and release formaldehyde, this weakens the glue bond. For this reason it is not considered waterproof but rather water resistant and is not used for marine plywood.
- Urea Formaldehyde must be used in a well ventilated area because uncured resin is irritating and can be toxic. This is not unique as most uncured modern adhesives carry strong warnings.

It is not recommended to use of UF resins for exterior applications. So following are methods by which harmful formaldehyde emissions can be reduce by replacing few parts of UF by starch and then by using cross linkers for these blend systems.

3.1.1. Blending of Starch with UF Resin Adhesive

UF resin was reactively blended with various concentration of starch [46], esterified starch [47] [48] [49] and oxidized starch [50] as wood and wood composite adhesive. It is found that new system with UF-starch blending has advantages of low brittleness, low formaldehyde emission and water resistance characteristics. In esterified-starch blended UF adhesive strength found to be comparable with synthetic resin adhesive system and content of free formaldehyde was lower than 0.3% [47] [48] [49]. Oxidized starch blended UF resin adhesive has good chemical stability, insulating properties, temperature resistance, aging resistance, oil resistance and mildew resistance and environmentally-friendly starch adhesive has no harm to the human body and can be applied to wood adhesion [51] [52] [53]. UF resin and modified starch mutual react and form a net structure, water resistance of starch glue was improved, and drying time was shortened [54] [55] [56] [57]. So ultimately in above all systems few parts of UF were replaced by starch, because of which formaldehyde emissions were reduced and cost is maintained.

3.1.2. Addition of Cross-Linker in Starch-Urea Formaldehyde Blends System

UF-Starch blended adhesives were modified with different cross-linkers for improvement in performance properties. Starch adhesives were modified by isocyanate as cross-linker [58] [59] [60] [61] [62] [70] as well as starch adhesive with polyvinyl alcohol, borax, and carboxy methyl cellulose as system [63] [64] [65] [66] for wood composite can be prepared with isocyanate as cross-linker, influence factors on the bonding strength and water resistance of starch adhesive were studied by different solid content, adding isocyanate and additives like PVA, Acrylic emulsion. Bonding strength and water resistance were improved significantly by adding additives and isocyanates to starch. An environmentally friendly wood adhesive was developed by cross-linking cornstarch-UF blend system with hexamethoxymethylmelamine. It exhibited excellent mechanical properties comparable to many of the commercially available urea-formaldehyde plywood adhesives used for interior applications [67]. So by above all systems not only reduced formaldehyde emissions were achieved but improved water resistance and improved performance properties were also achieved and

cost is also maintained.

3.2. Alternative for UF/MUF Resin Adhesive for Wood/Wood Composite

Different studies on starch adhesives proved that it can be used as alternative for conventional amino resin (UF, UMF, PF) adhesives which is been discussed follows.

3.2.1. Modification of Starch Using Different Types of Cross-Linkers

Environment friendly Starch adhesives can also totally replace UF adhesives for wood and wood composite application. By addition of cross-linkers like isocyanates [68]-[76], Melamine formaldehyde with which water resistance, extremely low formaldehyde emission and comparable performance properties can be achieved. In other study it was stated three different cross-linkers such as glutaraldehyde, glyoxal and dimethyloldihydroxyethyleneurea used in wood composites .

3.2.2. Modification of Starch by Acid

Citric acid, borax, sodium hypochlorite were utilized as oxidizing agents for starch and it was found to reduce the moisture sorption, the molecular movement and swelling at high relative humidity [77] [78]. Tapioca starch was chemically modified with urea or polyvinyl alcohol in the presence of borate as cross-linker and catalyst to reduce its water sensitivity [79] [80] [81] [82] [83]. The adhesive prepared by oxidation of the corn starch has good fluidity, milky white, fine and glossy appearance, and significantly improved dry strength and wet strength, good machining property and good water resistance [84]. Oxidation of starch by sodium hypochlorite under aqueous alkaline conditions with the aid of the catalysis of nickel sulphate at room temperature was investigated. Optimization of starch oxidation is desirable to achieve the highest initial tack and bonding strength. Under the optimum condition, 98.7% of the initial tack and 11.4 N/25 mm of the bonding strength were obtained respectively. The modified starch adhesive showed great potential for industrial application [85] [86] [87] [88]. Sodium dodecyl sulfate was also used to improve the performance of water resistance properties in starch-based wood adhesive [89].

3.2.3 Addition of Emulsion in Starch

A natural rubber (NR) latex and starch was added as an adhesive to synthesize the medium density fiber (MDF) board panels. The study was aimed on increasing the mechanical and physical properties of MDF by using NR latex and starch as an adhesive. The results of this study indicated that starch can be used as a viable alternative binder with NR latex [90]. Starch-grafted-polyvinyl acetate (starch-g-PVAc) and epoxy resin can be used as high cohesive energy component to improve the dry shear strength of the starch adhesive [91].

3.2.4. Blending with Biopolymer

Protein-starch composite [92] [93] tannin-starch composite [94] can also be

used for wood and wood composites adhesives which is eco-friendly system with zero formaldehyde emissions. Aldehyde hardeners like glyoxal, dioxal can be used for enhancement of properties.

3.3. Replacement of Synthetic Polymer by Starch in Polyvinyl Acetate Wood Adhesive

3.3.1. Physical Blending of Starch with Polyvinyl Acetate Emulsion

Synthetic polymers in water based systems like polyvinyl acetate are commonly used for wood and wood composite adhesive applications for various advantages like excellent strength performance, cost effective, non toxic etc. Few parts can be replaced by renewable biopolymer starch which is cost effective and having adhesive properties naturally. Various commercial adhesive with PVAc-starch blend for lamination is been used widely.

3.3.2 Starch Grafted Polyvinyl Acetate Emulsion Adhesive for Wood

Graft polymerization of vinyl acetate on waxy corn starch was done to prepare wood adhesive which can be used at room temperature giving excellent bonding performance [95] [96]. Graft copolymerization enhanced the thermal stability, which improved the bonding strength and water resistance. The improved properties were attributed to the modified microstructure of the graft-copolymerized starch-based adhesive [97] [98]. Therefore, Modified starch produced from graft polymerization with vinyl acetate and butyl acrylate has been tried to use as a wood adhesive [99]. Adhesives made of conventional materials when compared with biopolymer-based adhesives are usually too weak for practical use [100], so the structural strength of starch-based adhesive should be strengthened to achieve high performance as a wood adhesive. For improving the performance of a corn starch based bio-adhesive, corn starch graft glycidyl methacrylate (AS-*g*-GMA) adhesive was prepared [101].

3.3.3. Addition of MMT/SiO₂ in Starch Stabilized Polyvinyl Acetate Emulsion Adhesive

Silica nanoparticles and montmorillonite (MMT) were used to improve the bonding capacity of renewable starch-based wood adhesive in this study [102] [103] [104] [105].

3.4. Starch as Well as Filler Based Hot Melt Adhesive

The hot-melt adhesive consisting starch found to be less harmful, more environmentally friendly, involves reduced production costs [106]. Starch ethers and esters (e.g., starch acetate) can be subjected to further processing and used as a component in hot melt adhesives. The advantage of this type of material is that lower melting points can be achieved which assists both compounding and application to thermally sensitive substrates [107] [108] [109] [110] [111].

4. Future Prospects

The main reasons for the increasing interest in starch-based adhesives are the legislation and increasing interest in environmentally friendly adhesives. Most of

the thermosetting adhesive resins used today in the wood composite industries depend on petrochemicals. UF, UMF, PF are widely used in the wood composite industries and are formaldehyde emitting source. Society recognizes the protection of health and the environment and consequently the use of synthetic products as major environmental problems thus encourages the use of renewable natural resources. Starch is an ideal material for manufacturing of wood-composite adhesives due to low cost, high free hydroxyl content, easy processing and treatment. Starch based adhesives have a limited water resistance, but it can be modified by cross-linking of starch. A lot of research has already been done on modification and cross-linking of starch with synthetic materials. However, the challenge remains to produce the starch-based adhesive with high water resistance and fungal resistance similar like synthetic resin adhesives.

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