

AN ABSTRACT OF THE THESIS OF

Svetlana Peshkova for the degree of Master of Science in Wood Science
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Abstract approved _____

Kaichang Li

Wood adhesives are essential components of wood composites. At present, the commonly used wood adhesives, phenol-formaldehyde (PF) and urea-formaldehyde (UF) resins, are petroleum-based synthetic resins that may result in emission of formaldehyde in the production and use of wood composites. Because the world's oil reserves are naturally limited and formaldehyde is hazardous to human health, wood composite industries would greatly benefit by development of formaldehyde-free wood adhesives from renewable resources.

Marine organisms, such as mussels, produce adhesive proteins for binding to wet surfaces in seawater. Marine adhesive is a protein rich in 3,4-dihydroxy-phenylalanine (DOPA) and lysine residues. By means of a phenol-oxidative enzyme, the marine adhesive protein cross-links to form a tough and water-resistant polymer. Inspired by the strong adhesive properties of the marine adhesive protein, we investigated the possibility to develop a formaldehyde-free adhesive for wood composites using the marine adhesive protein as a model. Because the extracted and synthetic

marine adhesive proteins are expensive and not readily available, we focused our efforts on surrogates of the protein.

In this study, we investigated whether a polymer with a phenolic hydroxyl group or an amino group, the two key functional groups of the marine adhesive protein, could be converted to a wood adhesive system. First, we investigated poly(4-vinylphenol) (PVP), a polymer containing a phenolic hydroxyl group, as a key material for a wood adhesive. The aqueous suspension of PVP could be used as a wood adhesive to produce wood composites with the shear strength of up to 3 MPa. Addition of compounds with amino groups, such as 1,6-hexanediamine or diethylenetriamine, to the PVP suspension, resulted in a significant increase of the shear strength. When the molar ratio of the phenolic hydroxyl group in PVP vs. 1,6-hexanediamine was 3:1, the shear strength of wood composites bonded with PVP/1,6-hexanediamine could be twice as high as that with the aqueous PVP suspension alone.

Then, we investigated whether chitosan, a natural polymer with an amino group, could have a potential as a wood adhesive. We found that a chitosan-based wood adhesive system could bond wood veneers strongly when chitosan, a phenolic compound, and laccase were all present. Ten phenolic compounds with different chemical structures were studied. The adhesive strength of a chitosan-phenolics-laccase system was highly dependent upon the chemical structure of the phenolic compound used in the system. The shear strengths of wood composites made with the systems containing a phenolic compound with only one hydroxyl group were related to the system's viscosity and to the oxidation rates of the phenolic compounds by laccase. However, for the adhesive systems containing a phenolic compound with two or three phenolic hydroxyl groups

adjacent to each other, no correlations among shear strengths, relative oxidation rates of the phenolic compounds by laccase, and the viscosities were observed.

Results from this study reveal that a strong, water-resistant and formaldehyde-free wood adhesive could be developed through mimicking of marine adhesive proteins. Although the new adhesive systems worked on the same principles as marine adhesives, materials in the new adhesive systems did not have to be protein or polypeptides.

Development of Formaldehyde-free Wood Adhesives

by

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APPROVED:

Redacted for privacy

Major Professor, representing Wood Science

Redacted for privacy

Head of the Department of Wood Science and Engineering

Redacted for privacy

Dean of the Graduate School

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Svetlana Peshkova, Author

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DEVELOPMENT OF FORMALDEHYDE-FREE WOOD ADHESIVES

INTRODUCTION

WOOD COMPOSITES

History of development of wood composite panels

Veneers and plywood

The origin of veneers and plywood can be tracked back to thousands of years ago. As discovered from the tomb of Tutenkhamon, the ancient Egyptians used to make decorative veneers from expensive woods to conserve the wood and reduce the cost (Rinne, 1952). The wall painting named Sculpture of Thebes, dated around 1450 B.C, was the earliest revelation of veneer craftsmanship (Maloney, 1977).

In those early times, veneers were hand-made products prepared by manual sawing. Consequently, they were quite expensive. It was not until the end of the 18th century, when the first circular saw was invented, that production of veneer became more affordable for a large industrial use. However, the early circular saw had a thick blade that resulted in excessive wood waste. Thus, when in the 19th century the first rotary peelers enabled the production of thin wood slices, production of veneer became more economical. This technical advancement gave a boost for massive plywood production (Rinne, 1952).

In North America, the pioneer of commercial veneer manufacture was a company established in New York City in 1824. Later in 1905, the

first plywood panel for structural applications was developed in Portland, Oregon. Three decades after that, in 1934, water-resistant adhesives were developed for making plywood panels for exterior applications. The middle of 1930s is considered the birth time of the modern plywood industry (Maloney, 1977).

Board products from wood particles

An early document on particleboard, "Utilization of Wood Waste," occurred in Ernst Hubbard publication in 1887. The author proposed making a panel by hot pressing a mixture of sawdust and blood albumen between two platens. In 1905, an American inventor Watson used wood particles to create a board that resembled modern flakeboard. In the 1914, Carl G. Muench developed a panel product based on then existing papermaking technology. He built a production line similar to the one for paper manufacturing. Slurry of wood fiber in water was formed into a thick mat on a continuous conveyer belt. The water was drained through the conveyer mesh and the damp mat was oven dried. The product was an early fiberboard, which found extensive use in wall sheathing, paneling, and insulation.

There is no certainty where the first commercial manufacturing of particleboard started. During the World War II in 1941, the plant in Bremen, Germany, began its board fabrication using spruce chips and phenolic glues. At almost the same time, the American plant of Farley & Loetscher Mfg. Co. started the board production in the US.

The particleboard industry rapidly developed after World War II. For Europe lacked wood resources in the aftermath of the war. It was advantageous to utilize wood waste as a raw material. In addition, abundant sawmill wastes in the U.S. was stimulation for the wood composites industry in the North America.

With the breakthrough in hot press and resin technology, a dramatic increase in the panel manufacture in the U.S. started in the 1960s. Since that time, fiberboard and particleboard obtained their steady position in floor underlayments and furniture. The market for mobile home flooring was covered by urea formaldehyde (UF)-bonded particleboards. Some particle-based panels, such as flakeboard, were even accepted as a structural material. Until present, flakeboard is recognized for structural application in Canada.

In 1960, Willamette Industries established a plant in Albany, Oregon, to produce a new type of panel with a fine particle layer on the outsides and coarse particles in the core. This product, called Duraflake, provided a smooth surface and served as a perfect underlayment for plastics or veneers. Due to the durability, aesthetics, and large sizes of the panel, Duraflake became very popular in the furniture industry. Many more plants for this product were built in the northwestern part of the U.S. using Douglas fir wood as a raw material. It is worthy to note that the acid level in Douglas fir facilitated fast cure of UF adhesives used for bonding the panel (Maloney, 1977).

Wood and wood properties

Wood has been one of the first natural resources explored by human beings. Forests cover the biggest part of the planet; they are predominantly naturally grown and renewable.

Solid wood received the first recognition for its unique properties as a house-building material. Wood is lightweight, strong, and flexible. It has good thermal insulation properties. It is easy to work with and relatively inexpensive (Rinne, 1952). However, solid wood has also drawbacks. Wood is an anisotropic material, which means that it has different physical properties along the three perpendicular directions (Haygreen and Bowyer, 1996). Wood fibers have tendency to significantly shrink and swell in radial direction. The magnitude of the shrinkage and swell depends on the microfibril angle of S2 layer in the cell wall. The bigger the angle, the higher the dimensional changes. The fiber angle is larger in reaction wood than in normal wood. Presence of reaction wood adds even more unevenness into the properties of lumber. A board with reaction wood will warp and twist on exposure to moisture. Solid wood also contains knots. Knots are outcomes of tree branches that can run through a big part of the stem. Disrupting the grain direction of the bole, knots weaken strength of wood.

Types of wood composites

In the composite products, veneers, strands, particles, or fibers are arranged in certain way to produce a uniform structure. Panels made with veneer or lumber laminated parallel to the grain have a higher strength than whole wood boards due to minimization of knots and other wood defects

(Haygreen and Bowyer, 1996). Although, the random arrangement of wood particles or fibers would reduce the maximum strengths of some panels, when compared to strengths of solid wood in the grain direction, wood composites is a good solution to minimize or eliminate drawbacks of solid wood.

Plywood

The term “plywood” means combined wood. Each individual ply performs as a separate part of the assembly and improves the integrity of the whole structure (Maloney, 1977). The panels are formed by cross-laminating veneers. In this arrangement, the grain direction of neighboring plies is perpendicular to each other. Generally, an uneven numbers of plies are used to maintain balance of physical properties, although some plywood panels are produced with an even number of veneers, when two plies at the core are oriented with the grain direction parallel to each other (Rinne, 1952). Due to the alternation of the grain direction of the layers, plywood has the advantage of dimensional stability and equal bending strengths in both directions of the plane of the panel. Plywood board also offers a strong interface, which does not split or slide.

Modern plywood is bonded either with phenolic-based or urea-based resins. The resins are applied as water solutions through adhesive spreaders at a rate of 35 to 45 lbs per ft².

Laminated veneer lumber

Construction of laminated veneer lumber (LVL) is similar to that of plywood except that the veneer plies are oriented in the same grain direction. The uniform distribution of wood defects in LVL gives it higher strengths than solid wood (Haygreen and Bowyer, 1996).

Particleboard

By definition, a particleboard is a product made with wood particles that have been mixed with a bonding agent and pressed into a uniform panel. Commonly used particles include shavings, chips, flakes, strands, wafers, and sawdust. Currently in the U.S., the shavings make up one half of the wood particles used in the particleboard production. Mill residues and particles from roundwood are two other main sources of the raw materials. For the benefit of environmental protection, "urban wood" has been actively incorporated into the panel manufacturing (Haygreen and Bowyer, 1996).

Particleboard has a number of technical advantages over solid wood for specific applications. Low cost, smooth surface, and big sizes allowed the panels to successfully enter the flooring market (Maloney, 1977).

Unfortunately, particleboard swells in thickness more than solid wood. The expansion can range from 10 to 25% of the dry thickness of the panel with increase in its moisture content (Haygreen and Bowyer, 1996).

UF resin is the commonly used adhesive for the particleboard production. The content of UF resin in particleboards is about 6 to 10% by

weight. Particleboards intended to exposure of elevated moisture are produced with PF resins (Haygreen and Bowyer, 1996).

Oriented strand board

Oriented strand board (OSB) is made of three or five alternate layers of strands oriented at 90 degrees, utilizing the same principle as plywood. Many plants have machines that cut the strands from longwood. Aspen has been the preferred species for these products due to its low density, but other low-density woods, such as yellow poplar and sweetgum, are also being used. Phenol-formaldehyde resin is a typically used as an adhesive for this board, although isocyanate resins started being increasingly used (Haygreen and Bowyer, 1996).

Applications of wood composites

Plywood is divided into two main categories: structural and decorative plywood panels, depending on the wood species, types of adhesives, and quality of finishing.

Being a poor heat conductor and a light, strong material, plywood is an excellent resource for building construction. Softwood species is the major raw material for structural plywood. The panels are commonly used in sheathing, siding, and subflooring in houses. Other uses are found in kitchen cabinets and shelving, exterior panels, inside fitting, theaters, churches, railways, and ships as well as industrial items such as pallets, crates, and concrete forms.

Decorative plywood is an aesthetically pleasing product. Its face can be made from more expensive and attractive hardwood species. An interior grade adhesive system is used for producing these types of panels. Decorative plywood is used in constructions of furniture and interior wall panels.

LVL is mainly used for headers over garage doors and large windows, in I-beam flanges, and in scaffold planks (Haygreen and Bowyer, 1996).

OSB is also used as a structural panel. Its major application is in roofing and wall sheathing.

Particleboards are used for mobile home decks and underlayments for carpeted floors. About one-third of the board goes into making kitchen and stereo/TV cabinets (Haygreen and Bowyer, 1996). Traditionally, most of particleboard is glued with urea formaldehyde resins that do not possess waterproof properties. As a result, the majority of the boards have been designated for interior uses. In addition, there is a small production of particleboards bonded with phenolic resins that are known for their waterproof characteristics. Therefore, particleboard made with this adhesive is used for special exterior products such as exterior siding and sheathing. Furthermore, the panels bonded with phenolic resins are utilized in the furniture manufacture, where secondary processing requires high temperature and long pressing time. Urea-based adhesives decompose under these harsh conditions, while phenolic glues work well (Maloney, 1977).

Due to the molding technology that allows making a wide range of shapes with smooth edges and silky surface, molded particleboard found its application as furniture parts, sheet goods, and tiles. Shaving-type particleboard is suitable for floor underlayment and it is placed over rough sub-floors to provide a smooth surface (Maloney, 1977).

Environmental effects of the wood composites manufacture

There are many environmental benefits for production of particleboard and fiberboard from wood wastes of sawmills and furniture plants. For example, not only the waste material is reduced but also the pollutants from burnt wood are eliminated.

Modern composites manufacturing plants may be cleaner and technically superior than ever before. However, the manufacturing processes are still negatively impact the environment.

Open storage facilities for wood particles cannot contain the small particles from spreading over to the adjacent localities. Extractives leaching from the wood material pollute the surface and ground waters. Released gases from dryers and vapors from resin blenders create an offensive odor around the plant area. Smoke from waste burners, volatile solvents and hydrocarbons from the board finishing lines pollute the air. Formaldehyde emitted from the hot press is a health hazard for the workers. Besides chemical contamination, there is a considerable noise pollution from the high-pressure blowers and pumps, and from sawing, milling, sanding, and drying equipment (Maloney, 1977). Designing an environmentally friendly manufacturing system is a challenge for the wood composites industry.

WOOD ADHESIVES

Evolution of wood adhesives

A wood adhesive is one of the major non-woody components in wood composites. The early wood adhesives include starch and protein-based adhesives such as casein, soybean and animal glues (Lambuth, 1983). In the beginning of the twentieth century, soy protein and blood were used commercially to produce plywood from softwood in the Pacific Northwest of the United States. Soy protein was modified with lime and salts of metals for improvement of moisture and microbial resistance of wood composites bonded with the soybean-based adhesives (Blomquist, 1983). During the same time frame, starch-based adhesives were used for production of indoor-grade plywood that was further assembled into furniture with animal (hide) glues. The starch-based adhesives have light color of glue lines and are easy to apply even on difficult joints. Because these adhesives had low resistance to moisture, they were restricted to wood composites used in dry interiors (Lambuth, 1989).

Phenol-formaldehyde (PF) adhesives were introduced at the beginning of the 1930s. Early PF resins were available in a film form in limited quantities. These adhesives required high temperature for proper curing (Blomquist, 1983). In the U.S., hot-pressing operations for manufacture of wood composites began around 1932; this novel technology facilitated application of PF resins in the wood composites industry. However, widespread application of PF resins in the production of wood composites did not begin until after 1945 when a liquid-form PF resin was developed (Lambuth, 1983). Not long after successful application of PF resins in production of wood composites, urea-formaldehyde (UF)

adhesives were brought in the production of furniture and hardwood plywood. PF, UF and resorcinol-formaldehyde (RF), the latter became available in 1943, were extensively used for producing military equipment in the World War II. During the war period, new melamine-formaldehyde and poly-vinyl acetate adhesives were developed. Shortly after the war, epoxy resins and polyurethanes were added to the line of wood adhesives (Blomquist, 1983).

Nowadays, enormous amounts of synthetic resins are spent annually for production of wood composites. In 1997 only in North America alone, about 1.6 million metric tons of wood adhesives were consumed. Among them, 94% consisted of formaldehyde-based resins and 6% of vinyl-based systems, isocyanates, and others (Sellers, 1999). In Europe, 160,000 tons of phenolic resins and 2.6 million tons of urea-formaldehyde/melamine-formaldehyde were used in 1997 (Roll, 1998). In China, the estimated demand for wood adhesives for the year 2000 was over 560,000 tons, the majority of which was urea-formaldehyde resins (Hse, 1999).

Theories of adhesion

By definition, an adhesive is a “substance capable of holding materials together by surface attachment” (Blomquist, 1983). An assembly formed with an adhesive consists of two objects, adherends, connected to each other by a layer of an adhesive material. Development of the bond between an adhesive and adherends is attributed to the joint actions of three forces: mechanical interlocking, physical attraction, and chemical bonding (Gollob and Wellons, 1990).

Mechanical interlocking results from the penetration of an adhesive into the wood fibers and subsequent crosslinking/solidification of the wood adhesive. For thermosetting adhesives, an adhesive in a liquid form flows easily into the pores of wood and then crosslinks/solidifies once heated, thus forming mechanical plugs (Gent and Hamed, 1983). For thermoplastic adhesives, an adhesive melts and flows into the pores of wood at high temperature, and then solidifies once cooled. It is proposed that a strong bond will develop only when an adhesive penetrates two to six fibers deep into the wood surface. The increase of the surface area for the molecular interaction between adhesive and wood fibers is an important factor for mechanical interlocking strengths (Gollob and Wellons, 1990). There is a hypothesis that roughening of adherend's surface will improve the bond strength because of the increased bonding area. This theory could be true for certain substrates, but is controversial for wood (Pizzi, 1994). In general, the mechanical interlocking mechanism is proposed for porous materials like wood, textiles, or paper. For impenetrable materials, such as metals and glass, other adhesive theories are more relevant (Gent and Hamed, 1983).

Physical attractions between wood and an adhesive include van der Waals forces, hydrogen bonds, and electrostatic interactions; they are also called physical adsorption or specific adhesion. The strength of individual van der Waals interaction, hydrogen bond, and electrostatic interaction is weak. However, great numbers of hydroxyl or other functional groups in wood components and adhesives are available for the physical attractions. Therefore, the physical attractions could collectively make major contributions to the adhesive strength of wood (Gollob and Wellons, 1990) (Pizzi, 1994). At present, many adhesive chemists indeed consider physical attractions the major adhesion forces in wood composites.

Chemical bonding is the formation of covalent linkages between wood and adhesive polymers (Gollob and Wellons, 1990). For a long time it was thought that extensive chemical reactions occurred between the adhesive and wood in the production of wood composites. However, the latest research has not been able to demonstrate the presence of substantial amounts of covalent linkages between wood and adhesives in the conventional wood composites (Johns, 1989). Lacking evidences of covalent linkages could indicate either the incapability of current detection methods or the presence of undetectable amounts of covalent linkages.

There is another type of chemical bond that has been demonstrated in wood adhesion. It is the metallic coordination bond. This is the linkage formed between metal ions and their chelators. In the case of wood treated with the preservative copper-chromium-arsenate (CCA), copper and chromium are capable of forming coordination bonds with electron-donating groups such as amide groups from UF resins or phenolic hydroxyl groups from PF resins. Interestingly, treated wood can either form significantly stronger or much weaker adhesive joint than an untreated wood (Pizzi, 1994).

Types of wood adhesives

Wood adhesives can be simply classified as adhesives from natural resources and synthetic resins that include thermosetting resins and thermoplastic resins. Properties and applications of major types of wood adhesives will be described as follows.

Natural glues

Animal glues

Animal glues are some of the earliest adhesive systems. These are natural polymers derived from the collagen of animal skin, connective tissues, and bones (Sellers, 1985). The key component of animal glues is proteins or polypeptides. Depending on sources, these proteins may have a different composition of amino acids. It is well established that viscosity, adhesive strengths, and other properties of proteins are highly dependent upon the interactions of functional groups of amino acids in proteins (Subramanian, 1983). Therefore, animal glues from different sources could demonstrate very different adhesive properties.

Proteins obtained from boiling animal skins or bones in water are sticky materials that turn into a gel on cooling. These protein-based adhesives can produce strong and biologically resistant bonding to wood. They were widely used for joining small veneers and woody parts such as for musical instruments. Nowadays, these glues are still used in furniture crafting, woodworking, and for adhesive paper tapes (Subramanian, 1983). However, these types of adhesives did not prove useful in plywood production due to their quick gelation. Besides, availability of these adhesives is highly dependent on the meat processing industry and cannot meet the demand for production of wood composites (Sellers, 1985).

Casein is another example of protein-based adhesives. It is obtained from milk and has higher content of carboxylic acid groups than the proteins from collagen. Therefore, casein can be easily dissolved in an alkali

solution. The commonly used casein-based adhesive is called casein-lime glue that is prepared by mixing calcium hydroxide with casein. Divalent calcium crosslinks the carboxylic acid groups in casein to form water-insoluble calcium caseinate. Some other polyvalent metal ions can also work as cross-linkers. Casein-based adhesives are used for making joints in exterior assemblies such as doors, beams, and arches. The joints are relatively strong, but are not very water-resistant. For example, when moisture content of wood composites bonded with casein-based adhesives reaches 18% and remains at this level for a long period of time, the composite panels lose their integrity (Subramanian, 1983). Before the appearance of the synthetic resins on the market, casein-based adhesives were extensively used for making laminated timber (Sellers, 1985).

Blood is a protein-based adhesive. It was prepared by spray-drying of soluble blood of domestic animals. The process was performed on specialized equipment that was available at no more than a dozen meatpacking facilities in the U.S. (Sellers, 1985).

Blood protein has a high amount of polar functional groups, but has a globular structure. Amino acids in blood protein are tightly held together through intramolecular interactions. As a result, unfolding the protein by dispersing it in an alkaline solution is essential for achieving the full adhesive strength. Blood adhesives were widely used in plywood manufacture. Blood was also used with soybean protein for water-resistant adhesive systems cured in a hot-press (Subramanian, 1983). Blood supply is directly related to the volumes of cattle, sheep, and hog butchered each year and its stable supply cannot be quarantined. Moreover, wood composites bonded with blood adhesives cannot meet current standards for structural panels (Sellers, 1985).

Plant glues

For almost 5,000 years soybeans, a native of eastern Asia, have been used as food. But it wasn't until the 1920s when it was used as an adhesive (Sellers, 1985). Soybean contains about 36 wt. % proteins (USDA, 2001). Almost 50 % of soybean proteins are present in a coil structure. An alkaline treatment helps unfold the proteins, thereby enhancing their adhesive strength. Polyvalent metal ions can also be used as cross-linkers in soy proteins to improve the water-resistance of wood composites (Subramanian, 1983). Soy protein-based adhesives are more durable than starch, but less moisture-resistant than casein. In addition, soy proteins are subjected to microbial degradation (Sellers, 1985). Therefore, preservatives such as pentachlorophenol are normally added to these adhesive systems. Major application of soy-based adhesives is for production of interior grade plywood.

Starch is a plentiful and inexpensive carbohydrate. Abundant hydroxyl groups in starch are able to form hydrogen bonds and van der Waals interactions with wood components. Therefore, starch is a strong adhesive for cellulosic materials such as paper. In the U.S., cornstarch is the most popular starch-based adhesive. At present, starch is widely used for gluing paper bags, paperboard, corrugated boxes, tapes, labels, envelopes, textiles, and wallpaper. However, products glued with starch are not water resistant because the hydrogen bonds and van der Waals interactions can be interrupted by water. Thus, starch cannot be used as a wood adhesive.

Synthetic resins

Synthetic resins can be simply divided into thermoplastic resins and thermosetting resins. They differ by their chemical structures and responses to heat.

Thermoplastic resins

Thermoplastic resins are polymers that soften and flow at elevated temperatures and solidify at low temperatures. Thermoplastic resins are also called hot-melt adhesives. Adhesive strengths with these thermoplastic resins are mainly from mechanical interlocking. Little chemical reactions occur when the resins undergo the heating and cooling process in the production of wood composites. No solvent is required for these adhesives. Therefore, there are no environmental concerns associated with organic solvents. A drawback for these systems is that the glue lines soften once exposed to heat. Wood composites bonded with thermoplastic resins also tend to creep. Commonly used thermoplastic resins include poly(ethylene-vinyl acetate), polyamides, polyvinyl acetate, and polyacrylate.

Ethylene-vinyl acetate copolymers (EVAc) are used in book-binding, carton sealing, carpet and shoes manufacturing. Thermoplastic resins like polyamides are favorably used in the furniture industry as edge fasteners. The above-mentioned resins are random copolymers, whose properties are controlled by the ratio of co-monomers. In contrast to the random copolymer, styrene-butadiene-styrene block copolymers offer thermoplasticity of styrene blocks and elasticity of butadiene units.

These are thermoplastic elastomers that offer high strength and flexibility of the glue line.

Polyvinyl acetate (PVAc), a homopolymer known as “white glue”, is another widely used thermoplastic adhesive. PVAc produces a durable and colorless glue line. PVAc can bond cellulosic material strongly and is popular in woodworking and in gluing paper.

Acrylic adhesives work through in situ polymerization of acrylic monomers. The esters of acrylic and methacrylic acids are the two most commonly used monomers for the polymerization. Since the polymerization of the acrylic monomers is inhibited by air, acrylic adhesives are suited for applications, where air does not penetrate easily, such as the threads of tightly fastened nuts and bolts. Another unique acrylic adhesive is based on the polymerization of α -cyanoacrylate. The monomer is so reactive that it polymerizes by moisture or water adsorbed on the adherend surface. Acrylic glues are mainly used for medical and surgical applications (Subramanian, 1983).

Thermosetting resins

Thermosetting resins are those that irreversibly cross-link upon heating and cannot return to the original chemical structure upon cooling. Thermosetting resins generally degrade if the heating is continued (Pocius, 1997). Major thermosetting resins for wood adhesives are phenol-formaldehyde (PF) resins and urea-formaldehyde (UF) resins.

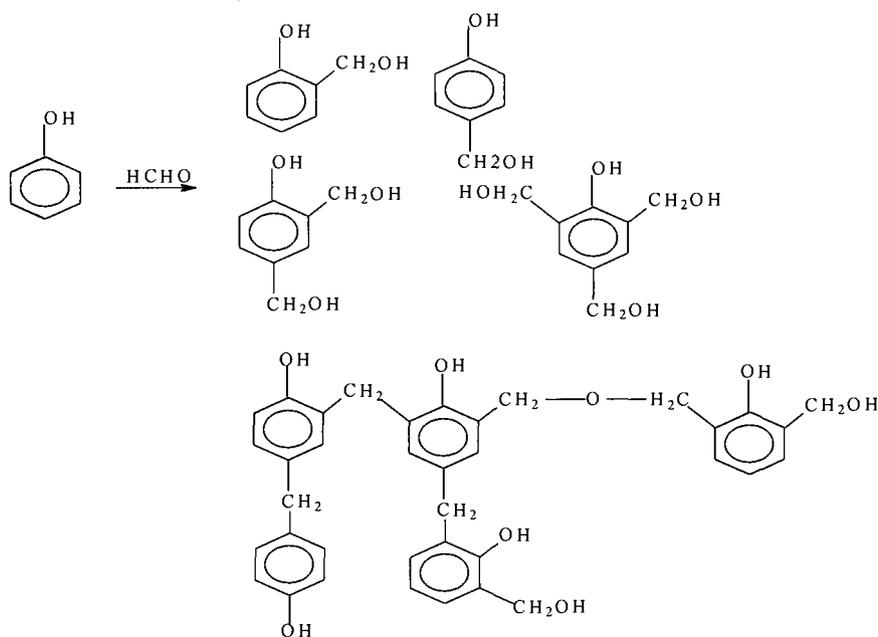
Phenol-formaldehyde resins

PF resins are one of the dominating wood adhesives. They are polymerization products of phenol and formaldehyde. The reaction is controlled by the pH of the solution as well as by the molar ratio of phenol to formaldehyde. First commercial production of the PF resins was done by the Union Carbide Corporation (Pocius, 1997).

Resoles

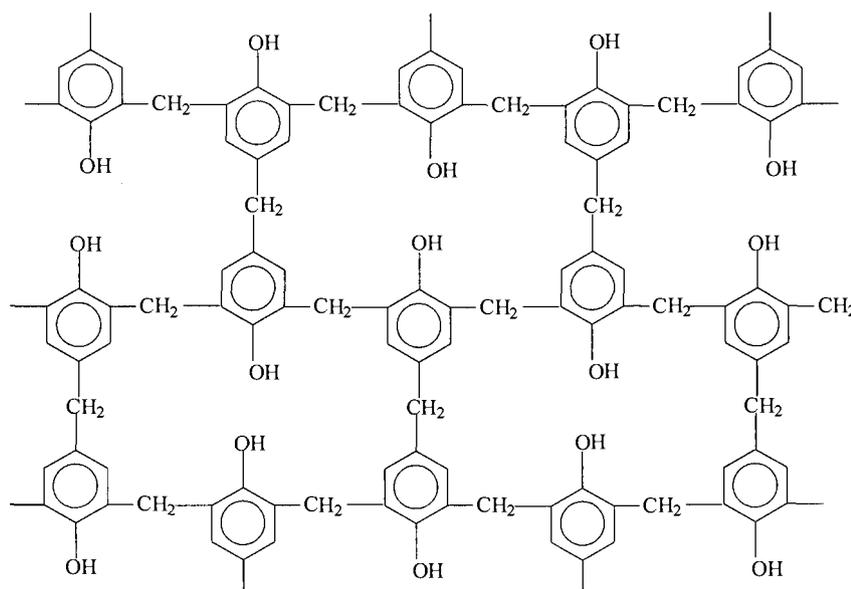
PF resins synthesized at alkaline conditions with excess of formaldehyde are called resoles. Catalysts, such as NaOH or KOH, are used in this synthesis (Pocius, 1997). During the first step, a reaction between phenol and formaldehyde occurs in ortho- or para- position of phenol. Excessive formaldehyde results in formation of di- or tri-methylol-substituted phenols (Fig. 1). Methylol-substituted phenols further react with each other to form a three-dimensional polymer network, where phenolic rings are connected through methylene or methylene ether (Fig.2). The structures of the polymer network depend on the reaction time, reaction temperature, pH value, and formaldehyde-to-phenol ratios. The formaldehyde/phenol ratio for synthesis of resoles varies from 1:1 to 3:1 (Subramanian, 1983). Unreacted methylol groups can further react with phenolic nuclei. In other words, the crosslinking reactions in resoles are a continuous process, which is a positive feature for the adhesive curing, but is undesirable for storage. To avoid premature cross-linking, resole PF resins are stored at a low temperature (Pocius, 1997).

Resole resins are the most commonly used PF resins in the forest products industry for production of plywood, particleboard, OSB and so on. They can be used in film, powder, or liquid forms.



Adopted from Adhesive bonding of wood and other structural materials (Subramanian, 1983).

Figure 1. Representative products in resole phenolic resins.



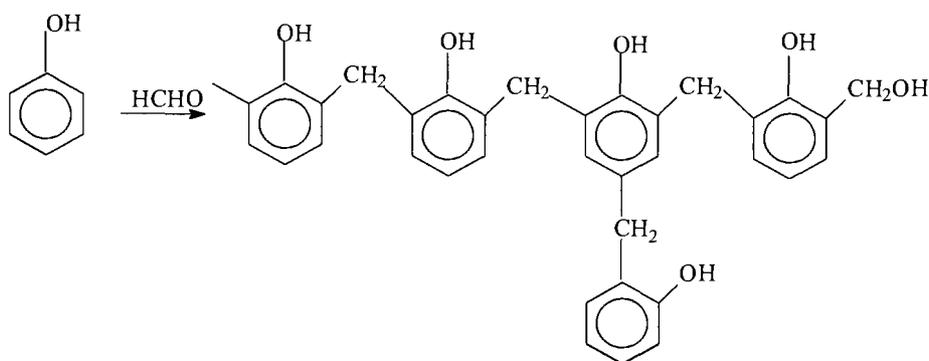
Adopted from Adhesive bonding of wood and other structural materials (Subramanian, 1983)

Figure 2. Illustration of a cross-linked structure of a phenol-formaldehyde resin.

Novolak

PF resins formed under acidic conditions with excessive phenol are called novolaks. Reactions of phenol and formaldehyde under these conditions yield methylol-substituted phenols. Under an acidic condition, the methylol groups are unstable and react further with another phenol. When bivalent metal acetates are used as catalysts, the phenolic nuclei are connected with methylene at the *ortho*-positions, thus forming a linear polymer (Fig. 3). Otherwise, the *para*-position of phenol also reacts with formaldehyde. Because excessive phenol over formaldehyde on molar basis is used in the synthesis of novolaks, there are no unreacted methylol

groups in the formed resins. Consequently, no further polymerization reactions occur in novolak, unless more formaldehyde is added. Novolaks have lower molecular weights than resoles. Commonly, paraformaldehyde is added to novolak resin prior to its use in production of wood composites (Subramanian, 1983). Paraformaldehyde will further react with phenolic structures in novolak polymers and form highly crosslinked network.



Adopted from Adhesion and adhesive technology (Pocius, 1997).

Figure 3. Synthesis of novolak phenolic resins.

Resorcinol, whose two phenolic hydroxyl groups are at 1,3-position in the aromatic ring, reacts much faster with formaldehyde than phenol. The reaction can occur at ambient temperature without any catalyst. Therefore, resorcinol-formaldehyde (RF) resins are first prepared at a low formaldehyde/phenol ratio (0.5 to 0.7) and then cured to form the adhesive bonds at ambient temperature with a further addition of formaldehyde, usually in form of paraformaldehyde (Subramanian, 1983). A hot-press operation is not needed for production of wood composites with RF resins. RF resins are equally durable as PF resins, but are five times more expensive than PF resins. As a result, they are less consumed and less

supplied (Sellers, 1985).

PF resins are used mostly for gluing exterior grade softwood plywood. The curing process is normally done at 130-150°C for a few minutes. In order to cure PF resins at a low temperature, an acid catalyst such as *para*-toluenesulfonic acid is needed. Unfortunately, acid damages wood fibers and consequently weakens the adhesive bonds. Therefore, reactive RF resins that can cure at room temperatures decrease the use of the acid-catalyzed PF resins (Subramanian, 1983).

Urea-formaldehyde and Melamine-formaldehyde

Urea-formaldehyde (UF) resins are polymerized products of urea and formaldehyde. These resins are well soluble in water, non-flammable, colorless, and adaptable to a range of curing conditions. Urea reacts with formaldehyde forming methylol derivatives that react further to produce linear and branched units. The commonly used molar ratio of formaldehyde to urea is in the range of 1.5 to 2.0. The pre-polymerized structures (Fig. 4) condense into a three-dimensional network with the addition of an acid catalyst. To reduce the acid damage of wood, mild organic acids such as tartaric acid or citric acid are used as catalysts (Subramanian, 1983).

Melamine reacts with formaldehyde to form bonds that are more resistant to hydrolysis than those bonds in the UF resins (Subramanian, 1983). Therefore, melamine-formaldehyde (MF) resins replace UF resins in certain applications where high stability of the wood composites to weathering is required. MF resins are more durable than UF resins, but they are more expensive as well. Addition of melamine to UF resins increases the durability of the latter.

Compared to PF resins, MF resins are less durable, but are more expensive, at least in the US. Available European technology allows reducing the cost of MF resins to the level of PF resins. Due to MF resins being less durable than PF resins, massive production of MF resins is held back in the US (Sellers, 1985). At present, MF resins are mostly used as a fortifying additive in UF resins for making interior laminate decking and finger joints.

Other thermosetting adhesives used in production of wood composites are polyurethanes, isocyanates, and epoxy-resins.

Applications of adhesives

According to application conditions for wood composites, wood adhesive systems can be classified into three categories: exterior application, interior water resistant application, and interior moisture resistant application.

When wood composites are used outdoors, they should be resistant to water, weather, microbial degradation and pressurized treatment with preservatives. Water-resistance of wood adhesives is one of the most

important qualities for production of exterior wood composites. There are only three types of adhesives accepted as waterproof; they are PF resins, RF resins, and at certain conditions the MF resins. In the US, most exterior structural plywood is made with PF resins. Exterior non-structural hardwood plywood is made with MF resins. Some special types of plywood, for instance marine grades, are made with RF resins.

The adhesives of interior-water-resistant grades are required to withstand temporary exposure to harsh environments such as elevated temperatures (over 50°C), water contact, or direct sun light. They are not required to perform well under such harsh conditions for a long period of time.

However, the glue lines should maintain their strength if the wood composites are only subjected to wetting and drying infrequently. UF resins are the most important adhesives of this grade and are widely used for production of plywood and particleboard for interior applications. Addition of melamine or resorcinol to the UF formulations improves its water resistance.

Adhesives of interior moisture resistant grades are required to retain the bond strengths if the wood composites are occasionally exposed to moisture. Thus, wood composites bonded with these adhesives are not recommended for use in environments with a high humidity or with direct exposure to water. UF resins are normally used for these applications. Casein, soybean, and blood glues also fall into this category (Sellers, 1985).

Concerns associated with synthetic resins

Petroleum-dependence

Phenol, formaldehyde, and urea are the key raw materials for the mostly consumed wood adhesives. Formaldehyde is made from methanol. Urea is produced from ammonia and formaldehyde. Ammonia and methanol are obtained from natural gas, whose supply depends on gas reserve and its exploration. Use of natural gas as a fuel and its consumption by other industries affect its availability and price for production of formaldehyde and urea. In addition, enormous demand of urea as a soil fertilizer may influence the availability and the price of urea.

Phenol is produced from benzene that is derived from petroleum. Most of petroleum is used as a transportation fuel. As the world's population continues to grow, consumption of the fuel also increases, which will inevitably influence availability of this resource for the manufacture of phenol (Sellers, 1985).

We heavily depend upon petroleum for energy and use it as a raw material for thousands of industrial products. However, petroleum reserve is naturally limited, which means that we will eventually use up the petroleum. In addition, about two third of the oil reserve is found in the politically unstable Middle East. Thus, oil supply has been volatile for a long time. Use of alternative sources of raw material for making the wood adhesives are essential to protect the wood composites industry from being dependent on petroleum. Therefore, the wood composites industry will greatly benefit from development of wood adhesives from renewable resources.

Formaldehyde emissions

Phenol-formaldehyde, urea-formaldehyde, and melamine-formaldehyde are predominant adhesives for production of wood composites. The formaldehyde emission from a composite panel glued with UF resins was first reported in 1962 (Marutzky, 1989). Since then, numerous studies have been done to investigate effects of this volatile chemical to human health. Although formaldehyde is widely used in several medical applications, some individuals are highly sensitive to it. Formaldehyde causes eye and respiratory tract irritation to humans. Exposure to formaldehyde gas triggers nasal tumors in rodents. Consequently, the committee of European Community and the U.S. Environmental Protection Agency pronounced formaldehyde a possible human carcinogen (Marutzky, 1989). Therefore, numerous studies have been directed to development of adhesive systems with low formaldehyde emission or being totally formaldehyde-free.

Research efforts in development of formaldehyde-free wood adhesives from renewable natural resources

Modern research in wood adhesives is focused not only on improvement of the bond strength, increased weather and moisture resistance of existing adhesives, but also on development of formaldehyde-free adhesives from renewable resources.

Tannins, natural polyphenolic compounds, were studied to replace phenol or resorcinol in PF and RF resins. Tannins-hexamethylenetetramine (hexamine) system could also be used as a formaldehyde-free adhesive for particleboard. Hexamine, which has been known as a tannin hardener since

1952, gelates tannins faster than formaldehyde. Particleboard made with this system emitted formaldehyde in a similar amount as heated solid wood. However, there are some obstacles for commercialization of this system. One of them is the fast gelation of the tannins-hexamine systems. The fast gelation prevents the adhesive from flowing and penetrating into the wood, which is necessary for the proper adhesive distribution and strong adhesion. Addition of surfactants and other agents are under investigation to improve the flow of the system (Pizzi, 1998). Extensive research is still under way to commercialize tannin-based wood adhesives (Roll, 1998) (Stracke and Roll, 2000).

Lignin is the second most abundant renewable natural resource. Lignin has been used to replace phenol in PF resins because of its abundance and low cost. In some PF formulations, lignin can replace up to 35% of phenol. The most commonly used lignin preparation is the spent liquor of a pulping process. At present, lignin-based wood adhesives still require the use of formaldehyde.

In search of new raw materials for adhesives from renewable resources, wood was liquefied for preparation of resole-type phenolic resin. Wood chips and wood flour can be liquefied, i.e. be converted into fluid material, at 250 °C without a catalyst or at around 150 °C with an acidic catalyst in an organic solvent. Two major methods are known for this process, first is with phenol, second with polyhydric alcohols. The liquefaction process transforms wood into reactive molecules that can further react with present phenol and polyols. Liquefying wood chips with phenol gives resole-type phenolic adhesive. Acceptable bond strength and water resistance for wood composites bonded with this type of adhesive could be obtained when wood composites are produced at 120 –130 °C for

30 seconds. Remarkably, the pressing temperature is 15 °C lower than the one used for typical resole adhesives (Shiraishi and Yoshika, 1998).

Starch is another very appealing biopolymer for adhesive chemists. This renewable, biodegradable, and inexpensive material was tried in combination with polyacrylic acid to produce a thermosetting adhesive. There is a potential that the adhesive system can be used in composites with natural fibers (Humphreys and Solarek, 2000).

There is a renewed interest in the use of soybean proteins as wood adhesives. Extensive research has been done on using soy products as additives to PF, PRF, and PMDI, for production of plywood and OSB. Some efforts have also been spent on improving water-resistance properties of wood composites bonded with soy proteins alone (Sellers, 1999; Vijayendran and Clay, 2000; Kuo and Stokke, 2000; Sun and Zhong, 2000).

Nontraditional approach to develop a new type of adhesives was taken by observing behavior of marine inhabitants. Sea mussels and barnacles secrete proteins that allow them to adhere to a variety of inert surfaces under water. This phenomenon prompted multiple attempts to learn and utilize the chemistry of the marine proteins for medicinal and industrial purposes.

Mytilus edulis, the most studied mussel, secretes byssus, a proteinaceous matter that looks like a bundle of threads with an adhesive plaque at the end. The adhesive plaque consists of a 3,4-dihydroxyphenylalanine (DOPA) -rich protein. Chemical characterization of this protein revealed that it is made of repeated decapeptides. Each decapeptide has one to two residues of DOPA, two residues of lysine, one

to two residues of trans-4-hydroxyproline, and one residue of trans-2,3-cis-3,4-dihydroxyproline (Deacon et al., 1998). The polyphenolic protein is highly basic and has an average weight 125,000. In the protein, 90% of the amino acid residues are lysine, hydroxyproline, alanine, serine, threonine, proline, tyrosine, and 3,4-dihydroxyphenylalanine (DOPA) (Waite et al., 1985). The protein is produced together with an oxidative enzyme. The enzyme is somehow activated after the DOPA-rich protein is secreted. The enzyme first oxidizes tyrosine residues in the protein to DOPA residues and then further into quinones, the cross-linking agents of the mussel adhesive protein (Rzepecki et al., 1992).

It was proposed that the secondary structure of the protein consists of no more than 5% α -helix, 10% β -sheet, 20% of β -turns, and the remaining part is a random coil. In a dilute solution, the DOPA-rich protein has a structure of a semi-flexible rod, where rigid and flexible chains alternate. At the $\text{pH} < 7$, the conformation is unfolded due to the electrostatic repulsion of the segments with positive charges. It is thought that this conformation allows the adsorptive interactions with other molecules and acts as a mucoadhesive. When the $\text{pH} > 7$, the protein aggregates as a result of auto-oxidation of DOPA into quinones and subsequent crosslinking with the lysine residues. The conformation and adhesive properties of the DOPA-rich protein in dilute solution are analogous with those of chitosan. Chitosan, a cationic polymer, assumes a flexible rod conformation and is able to adhere to various surfaces (Deacon et al., 1998). Adhesives with chitosan as the major component were able to glue glass (Yamada et al., 2000). However, little has been published on investigation of chitosan as wood adhesives.

Since 1985, methods for extraction of mussel adhesive protein from the mussel gland have been studied. Production of a large quantity of mussel protein through extraction is difficult and costly. Benedict and Picciano (1989) studied extracted mussel protein in conjugation with catechol oxidase as a cross-linking agent for the potential repair of living tissue. They demonstrated that a proper ratio of mussel adhesive protein and a cross-link catalyst could be successfully used for ocular tissue bonding.

Recombinant DNA technology is another way of obtaining derivatives and analogs of mussel adhesive proteins. Strausberg et al. cloned the genes encoded mussel adhesive protein and expressed the marine adhesive protein in *E. coli*. The recombinant protein was able to glue glass and plastic. The authors used mushroom tyrosinase for conversion of tyrosine residues to DOPA and observed quinone-lysine cross-linking reactions (Strausberg et al., 1989).

Because marine adhesive proteins are not readily available and synthetic polypeptides are expensive, in this study we investigated whether a non-proteinic polymer containing one of the key functional groups in marine adhesive protein could be used to develop a wood adhesive.

INVESTIGATION OF POLY(4-VINYL)PHENOL AS A WOOD ADHESIVE

*Svetlana Peshkova and Kaichang Li**

Department of Wood Science and Engineering, Oregon State University,
Corvallis, OR 97331

Wood and Fiber Science

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ABSTRACT

An increasing concern about the effect of emissive VOC, especially formaldehyde, on human health has prompted a need for more environmentally friendly adhesives. Mussels stick to rock or other substances very strongly in seawater through secreting phenolic protein adhesives, termed marine adhesives. The marine adhesives are formaldehyde-free and environmentally friendly. However, the marine adhesives are not readily available. In this study, we investigated whether a polymer, poly(4-vinylphenol) (PVP), containing phenolic hydroxyl groups, but no peptide linkages, could be used as a wood adhesive. The shear strength of wood composites bonded with an aqueous suspension of PVP could reach up to 3 MPa. Addition of 1,6-hexanediamine or diethylenetriamine to the aqueous suspension of PVP resulted in a significant increase of the shear strength. When the molar ratio of the phenolic hydroxyl group in PVP vs. 1,6-hexanediamine was 3:1, the shear strength could be twice as high as when the aqueous suspension alone is used. Curing mechanisms of PVP and 1,6-hexanediamine / diethylenetriamine are believed to be the same as those found in the naturally occurring quinone-tanning process. The adhesion mechanisms by which marine adhesives bond mussels to rock could be applied to development of a formaldehyde-free wood adhesive system.

KEYWORDS

Poly(4-vinylphenol), wood adhesive, quinone tanning, marine adhesive.

INTRODUCTION

A wood composite is primarily made up of wood of small dimensions (fibers, chips, strands, etc.) and an adhesive. Increasingly, the wood component may consist of recycled wood fibers and even branches. The production of a wood composite can be simply described as follows. Solid wood is first fragmented into small pieces such as strands and chips, and adhesive (a binder) is then added. After hot pressing, a wood-like product is formed. In this process, adhesive is one of the major non-woody components. The most commonly used wood adhesives today are phenol-formaldehyde and urea-formaldehyde resins.

It has been well documented that hazardous compounds, so termed volatile organic compounds (VOC), are emitted during the production and/or use of wood composites (Henderson 1979; Meyer et al. 1986; Marutzky 1989; Baumann et al. 2000). An increasing concern about emissive VOC, especially formaldehyde, to human health has generated a need for new, environmentally friendly adhesives.

As we know, mussels bind strongly to rock or other substances in seawater by secreting byssus (proteins) (Waite 1983; Rzepecki and Waite 1991). Studies have revealed that the byssus consists of a bundle of threads that end on an adhesive plaque and can be simply classified as three morphologically distinct regions, proximal portion, distal portion, and attachment plaque (Qin et al. 1997). The byssal threads attach to hard surfaces through the attachment plaque and merge with a stem that is deeply rooted in the base of the mussel foot. Because of its strong and opportunistic attachment to wet surfaces, the attachment plaque is the most intriguing part of the marine adhesive protein. Studies on many marine

mussels, belonging to the family Mytilidae, have thus far revealed that the attachment plaque consists of polyphenolic proteins containing 8-18 mol % 3,4-dihydroxyphenylalanine (DOPA) (Rzepecki and Waite 1991; Rzepecki et al. 1992). For example, the marine adhesive protein isolated from the common mussel *Mytilus edulis* is predominately composed of a decapeptide (Ala-Lys-Pro-Ser-(Tyr/DOPA)-Hyp-Hyp-Thr-DOPA-Lys) (Waite 1983; 1987). It has been demonstrated that this decapeptide may repeat up to 80 times in the marine adhesive protein and is a key sequence for the adhesive properties (Waite 1983). Because there is no genetic codon that directly encodes DOPA residues in nature, DOPA residues are believed to derive from 3-hydroxylation of tyrosine by a tyrosinase in a post- or co-translational process. When the byssal threads are secreted by the mussel feet, they are soft and colorless at the beginning and then gradually harden and turn brown. This process has been defined as quinone-tanning (Lindner and Dooley 1976; Lindner 1984; Waite 1990). The freshly secreted byssus contains not only a DOPA-containing protein but also a catecholoxidase that oxidizes catechol to quinone (Waite 1985). It is believed that catecholoxidase, somehow activated after the secretion of the DOPA protein, is responsible for the hardening and browning (Waite 1985). The quinone-tanning is a very complex process that includes various oxidation reactions and cross-linking reactions among tyrosine/DOPA residues and between tyrosine/DOPA residues and other amino acids such as lysine (Waite 1990). Quinone-tanned adhesives and varnishes have been comprehensively reviewed (Waite 1990; Rzepecki and Waite 1991).

Various DOPA-containing proteins or polypeptides have been prepared and studied as water-resistant adhesives (Yamamoto and Hayakawa 1979; 1982; 1982; 1982; Yamamoto 1987; 1987; 1989; 1989; 1996; Yamamoto et al. 1996; Yu and Deming 1998). These extensive

studies have revealed that “functionality, and not amino acid sequence, was the only feature necessary for moisture-resistant adhesion” (Yu and Deming 1998). Inspired by the strong binding of mussel adhesives, we investigated whether a polymer, other than a protein or a polypeptide, that contains a phenolic hydroxyl group could be a good adhesive for formation of wood composites. In this paper, we demonstrate that poly(4-vinyl)phenol can bond maple veneers very strongly in the presence of 1,6-hexanediamine.

EXPERIMENTAL PART

Materials. Poly(4-vinylphenol) (PVP) (an average Mw, 20,000), 1,6-hexanediamine (HDA), and diethylenetriamine (DETA) were purchased from Aldrich. Other chemicals were also purchased from commercial sources. Sugar maple veneer with the dimension of 2500 mm long, 1270 mm wide, and 0.64~0.76 mm thick was a gift from State Industries (Eugene, Oregon). A commercial phenol-formaldehyde (PF) glue mix for laminated veneer lumber (LVL) was a gift from Georgia-Pacific resins, Inc. (Albany, Oregon). Laccase was a gift from Novozymes, Inc. (Davis, California).

Enzyme assay. Laccase activity was determined through monitoring the oxidation of ABTS [2,2'-azinobis(3-ethylbenzothiazoline-6-sulfonic acid)] (500 μM) at 420 nm ($\epsilon_{\text{max}} = 3.6 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$) (Li et al. 1998). The determination was made in a 50 mM sodium tartrate buffer (pH 4.5) at 30°C. One enzyme unit (U) was defined as 1.0 μmol of product formed per min under the assay conditions.

The differential scanning calorimetry analysis. Calorimetric measurements were obtained on a DSC-2920 (TA Instruments, Inc) with

argon as a purge gas. Argon flow was adjusted to a rate of 40 ml/min. The calorimeter was calibrated against indium (m.p. 156.6°C, $\Delta H=28.45$ J/g) at 10 °C/min. Test samples of ca. 2-5 mg were weighed in standard aluminum pans and closed with the lids. An empty aluminum pan with the lid was used as a reference. For the 1st runs, the samples were first cooled to 3 - 5°C with ice and the thermograms were then recorded at a heating rate of 10 °C/min between 5 to 300 °C. For the second runs, the samples at the end of the 1st runs were cooled to 3-5 °C with ice at an approximate rate of 50 °C/min and the thermograms were recorded again at a heating rate of 10°C/min between 5 to 300°C. The Universal Analysis V3.3B software supplied by TA Instruments, Inc. was used to plot and analyze the thermal data. The DSC spectra have been normalized to represent 1 gram of the samples.

Preparation of PVP suspensions. PVP (400 mg) was added to water (1.0 ml), stirred for 5 min at room temperature, and then used for bonding maple veneers. When HDA or DETA was used as an additive, HDA or DETA with a predetermined molar ratio between the phenolic hydroxyl group in PVP and HDA or DETA was added to the PVP suspension (400 mg/ml H₂O), stirred for 5 min at room temperature, and then used for bonding maple veneers. The repeating unit (C₈H₈O, the formula weight of 120) of PVP was used to calculate molar content of the phenolic hydroxyl groups in PVP. Laccase (65 U, ca. 205 µg) was added as a separate additive to the aqueous PVP suspension (400 mg/ml H₂O), stirred for 5 min at room temperature, and then used for bonding maple veneers. In an independent experiment, oxygen gas was bubbled in the aqueous PVP suspension for approximately 30 min at room temperature, and the suspension thus generated was used as a wood adhesive.

Evaluation of PVP preparations as wood adhesives. Various PVP preparations were evaluated for their abilities to bond two pieces of sugar maple veneers using Automated Bonding Evaluation System (ABES) (Humphrey 1999). The bonding area was 100 mm² (5 mm x 20 mm). The press pressure was 200 Psi with various press temperatures and press times. The bonding strength reported here is the basic lap-shear strength of the bond between two pieces of maple veneers.

RESULTS

We first investigated PVP as a wood adhesive. PVP swells and forms a suspension in water. We have determined that 400 mg of PVP in 1 ml of water is an optimum concentration for the shear strength of the resulting maple composites (data not shown). The effect of press temperatures and press times on shear strengths is shown in Figure 5. Shear strengths of the maple composites bonded with PVP at 80 °C were much lower than those bonded at other temperatures, whereas press temperatures of 100 °C, 120 °C, and 150 °C resulted in shear strengths that were comparable as long as press time was greater than 100 seconds.

Various additives were added to the PVP suspension, and their influences on shear strengths are shown in Figure 6. When press time was shorter than 275 seconds, adding a phenoloxidase laccase to the PVP suspension and bubbling O₂ in the PVP suspension each resulted in slightly lower shear strengths than that of the PVP suspension itself. When press time was 275 seconds, adding laccase or bubbling O₂ had little effect on shear strengths. When HDA or DETA was added to the PVP suspension, the shear strength of the resulting maple composite was much higher than

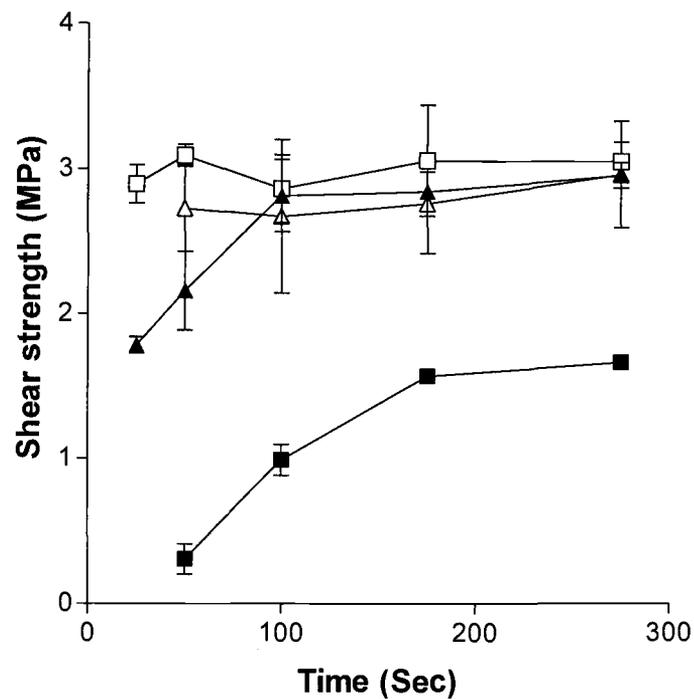


Figure 5. Shear strengths of maple composites bonded with a PVP suspension (400 mg/ml H₂O) at various press temperatures and press times. 80°C (■), 100°C (▲), 120°C (□), and 150°C (△). Data are the means of six replicates, and the error bar represents the standard deviation.

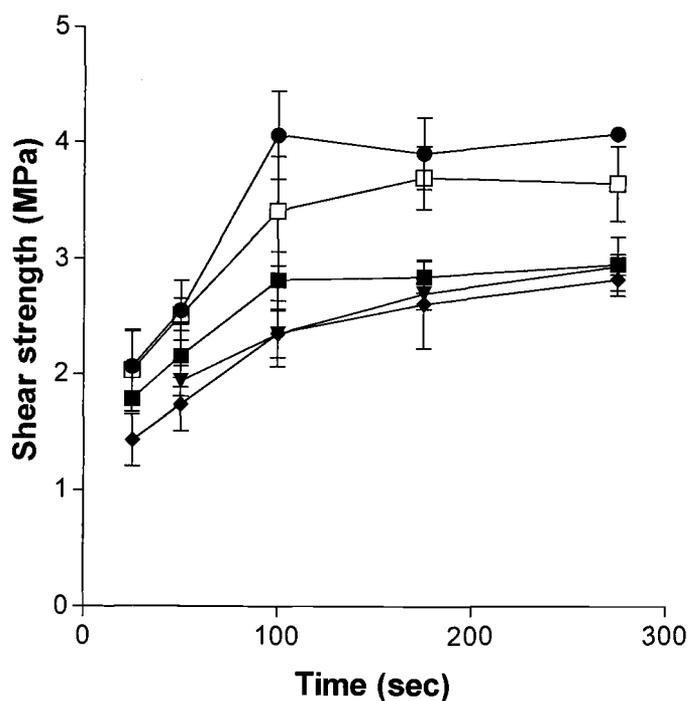


Figure 6. Shear strengths of maple composites bonded with a PVP suspension (400 mg/ml H₂O) in the presence of various additives at the press temperature of 100°C. PVP (■), PVP + O₂ (▼), PVP + laccase (◆), PVP + HDA (the molar ratio of PhOH in PVP vs. HDA, 6:1) (●), and PVP + DETA (the molar ratio of PhOH in PVP vs. DETA, 6:1) (□). Data are the means of six replicates, and the error bar represents the standard deviation.

that of composites made with the PVP suspension alone. Adding HAD yielded the highest shear strengths.

Inspired by the great effect of HDA in boosting shear strength, we further determined the effect on shear strength of the molar ratio of the phenolic hydroxyl group (PhOH) in PVP vs. HDA. From Figure 7, we can see that a molar ratio of 6:1 between PhOH in PVP vs. HDA gave rise to the highest shear strengths at the press time of 100 seconds, whereas a ratio of 3:1 resulted in much higher shear strengths than any other ratios at a press time of 275 seconds.

Figure 8 shows the effect of press temperatures on the shear strengths when the molar ratio between PhOH in PVP and HDA was 6:1. The press temperature of 150 °C appears to give the highest shear strengths, with 120 °C coming second. Interestingly, using a long press time (more than 100 seconds) at 120 °C negatively affected shear strength. When a ratio of 3:1 was used, the effect of press temperatures on shear strengths differed from effects when the ratio was 6:1 (Figures 8 & 9). With a ratio of 3:1, using a press temperature of 120°C resulted in much higher shear strengths than using 100 °C or 150 °C (Figure 9). At 100°C, shear strengths increased gradually with press time. At 120 °C, shear strengths increased sharply at press times of 25 to 100 seconds and then flattened out from 100 seconds on. At 150 °C, shear strengths were the lowest among the three press temperatures and increased very slowly when the pressing time was longer than 50 seconds. A commercial phenol-formaldehyde glue mix for production of laminated veneer lumber was used to bond the maple veneers at the recommended temperature of 105°C (Figure 9). Shear strengths of the maple composites bonded with a mixture

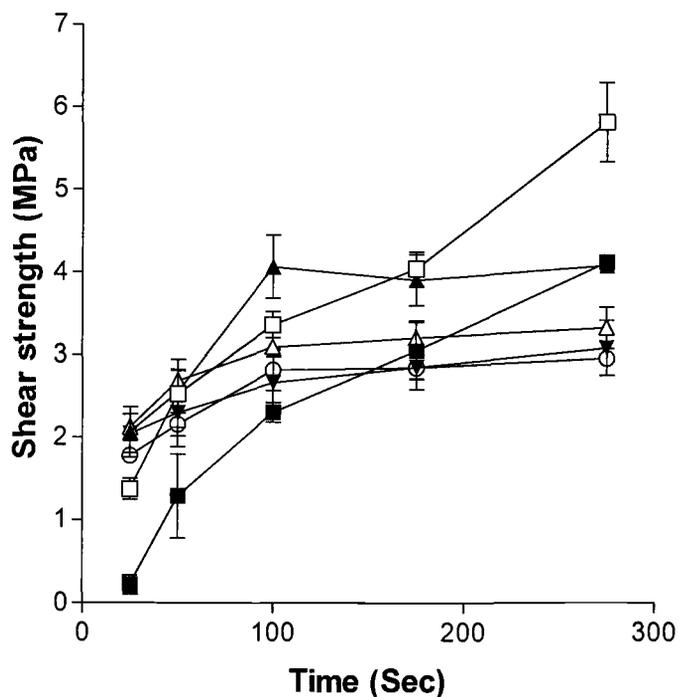


Figure 7. The effect of molar ratios between PhOH in PVP and HDA on shear strengths at the press temperature of 100°C. 2:1 (■), 3:1 (□), 6:1 (▲), 9:1 (△), 12:1 (▼), and PVP without HDA (○). Data are the means of six replicates, and the error bar represents the standard deviation.

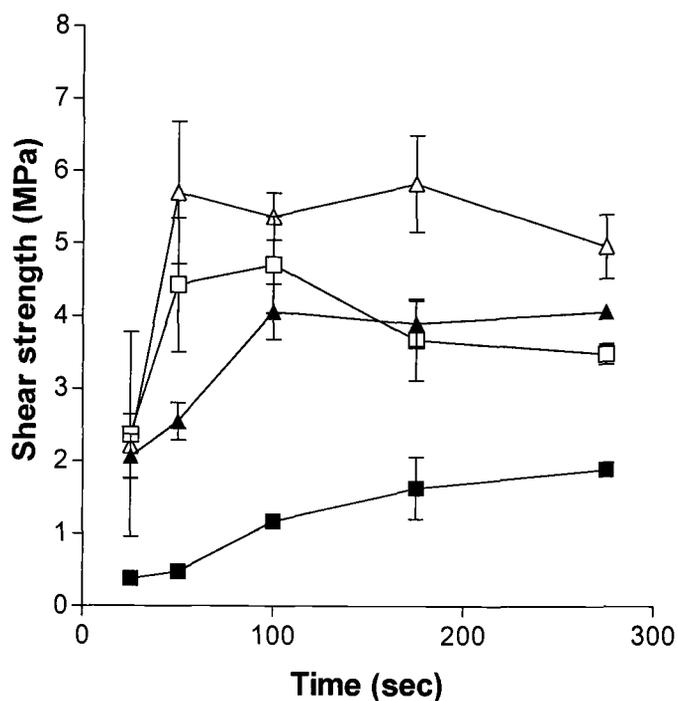


Figure 8. Shear strengths of maple composites bonded with a PVP suspension (400 mg/ml H₂O) in the presence of HDA with a 6:1 molar ratio of PhOH in PVP vs. HDA. 80°C (■), 100°C (▲), 120°C (□), and 150°C (Δ). Data are the means of six replicates, and the error bar represents the standard deviation.

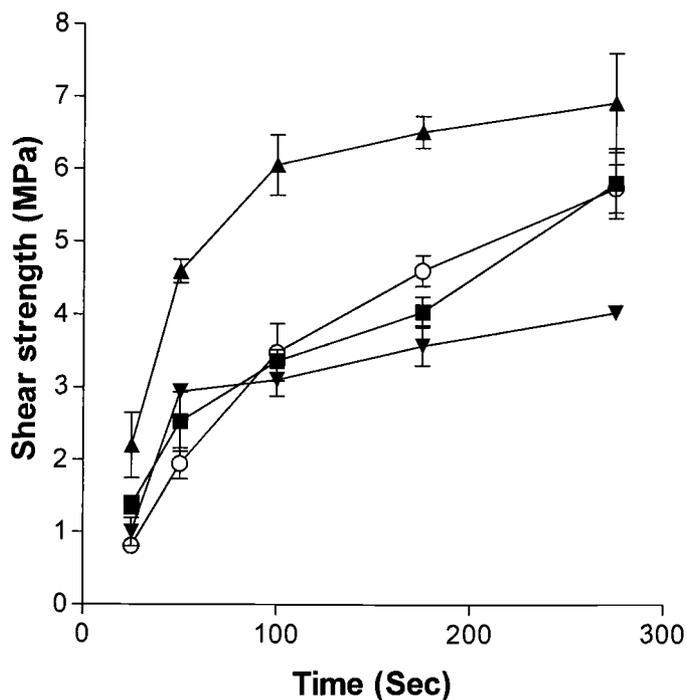
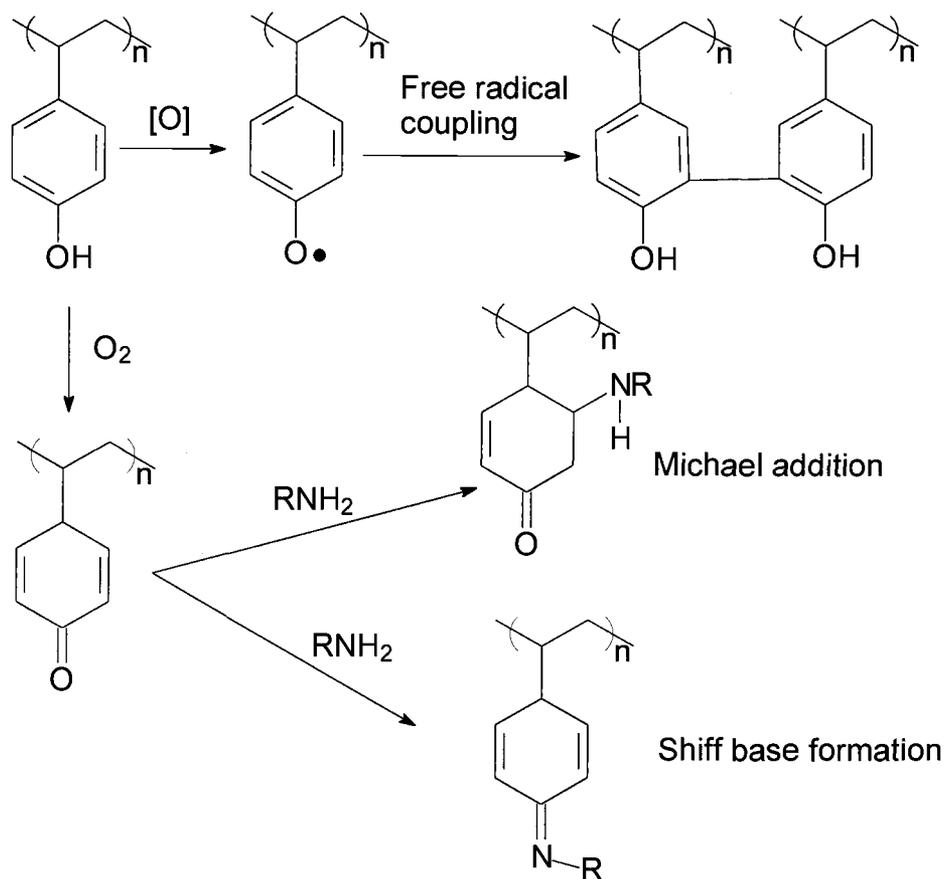


Figure 9. Shear strengths of maple composites bonded with a PVP suspension (400 mg/ml H₂O) in the presence of HDA with a 3:1 molar ratio of PhOH in PVP vs. HDA and with a phenol-formaldehyde glue mix for LVL. 100°C (■), 120°C (▲), 150°C (▼), PF glue mix at 105°C (○). Data are the means of six replicates, and the error bar represents the standard deviation.

of PVP and HDA at 100°C were comparable with those bonded with the commercial PF glue mix at 105°C (Figure 9). When the maple composites were produced with a mixture of PVP and HDA at 120°C, the shear strengths were much higher than those bonded with the commercial PF glue mix (Figure 9).

DISCUSSION

Phenol-formaldehyde (PF) resins and PVP both belong to a polymeric substance containing phenolic hydroxyl groups. The phenolic hydroxyl groups in both PF resins and PVP would form hydrogen bonds with wood components. Therefore, we believed that PVP should be able to bond wood veneers as PF resins do. From Figure 5, we can see that PVP did bond maple veneers strongly. It is known that the phenolic hydroxyl group (PhOH) is easily oxidized by oxygen, especially at elevated temperatures. Major possible reactions of PVP at elevated temperatures are shown in Scheme 1. When oxidized, PhOH is converted to a PhO• free radical that could couple with an adjacent phenolic free radical from a phenolic hydroxyl group in PVP or a phenolic substructure in lignin, thus crosslinking PVP or forming a covalent linkage between PVP and lignin. The PhO• free radical could also be further oxidized to a quinone if sufficient oxygen were present. Although reactions of a quinone with hydroxyl groups in wood could not be ruled out, contributions of such reactions to the crosslinking or the covalent linkages would be much less than those from free radical couplings. In other words, conversion of the PhO• free radicals to quinones would likely decrease the degree of the crosslinking of PVP, thus resulting in lower shear strengths.



Scheme 1. Major possible reactions of PVP and PVP/amines at elevated temperatures.

When the PVP suspension is saturated with oxygen, the phenolic hydroxyl groups on the PVP surface would be oxidized into quinones. This is why bubbling oxygen in the PVP suspension resulted in lower shear strengths (Figure 6). If the press time is sufficiently long, with the oxygen concentration being reduced, the crosslinking reactions might gradually prevail. This accounts for the comparable shear strengths for the PVP suspension and the O₂-saturated PVP suspension at a press time of 300 seconds. Laccase is a phenoloxidase that oxidizes phenol to a quinone via a phenolic free radical (PhO[•]). At present, it is still poorly understood that a PVP suspension pretreated with laccase resulted in lower shear strengths than the PVP suspension itself (Figure 6).

DSC spectra indeed indicate that some reactions occurred when PVP was heated (Figure 10). The heat absorption peak appears at about 90°C, which is consistent with results that the shear strengths at 80°C were much lower than those at other temperatures (Figure 5). When the PVP sample was heated second times, the heat absorption peak at about 90°C disappears. It is likely that the heat absorption resulted from reactions of PVP. It is worthy noting that the Aldrich catalog reports a glass transition temperature (T_g) of about 150°C for the PVP used in this study. If the T_g is 150°C, no significant flow of PVP will occur below this temperature, thus being no wetting and no adhesion. However the DSC spectra do not reveal a T_g at about 150°C. Moreover, visual inspection of the glue line indicated uniform distribution of PVP on the veneer surfaces at the press temperature of 100°C or higher. In other words, the PVP did flow. PVP swells in water well although it is not soluble in water. Water could also plasticize PVP, thus being partly responsible for the shear strengths shown in Figure 5.

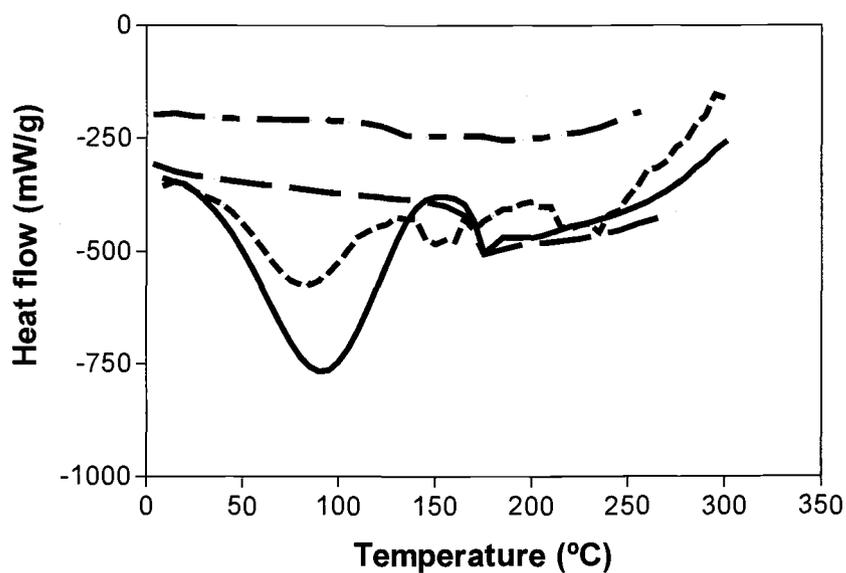


Figure 10. DSC characterization of PVP and PVP in the presence of HDA (the 3:1 molar ratio of PhOH in PVP vs. HDA). The 1st run of PVP (—), the 2nd run of the 1st-run-PVP (— — —), the 1st run of PVP + HAD (- - -), the 2nd run of the 1st-run-(PVP+HDA) (— - —).

It is well established that an amine readily reacts with a ketone or a quinone, a reaction known in nature as quinone-tanning (Waite 1990). Similarly, the phenolic hydroxyl group in PVP, when heated, is oxidized to a quinone that quickly reacts with an amine such as HDA or DETA via Michael addition reactions or Schiff base formation reactions (Scheme 1). Because HDA and DETA each have more than one amine group, they thus serve as effective cross linkers for the PVP. The DSC spectra show a heat absorption peak at about 85°C when a mixture of PVP and HDA was heated for the first time (Figure 10). However, the heat absorption peak disappeared when the pre-heated mixture of PVP and HDA was heated again (Figure 10), which implies the occurrence of some reactions when the mixture was heated for the first time. This quinone-tanning process may explain why the addition of HDA or DETA to the PVP suspension gave rise to much higher shear strengths than those of the PVP suspension itself. HDA is a small molecule and excessive HDA will concentrate at the adhesive interphase, thus causing a weak boundary layer and reducing bonding strength. If HDA levels in the PVP suspension were insufficient, the shear strengths would be low because of insufficient crosslinking. It is not clear at the moment why different optimum press temperatures were required for different ratios of PhOH in PVP vs. HDA.

CONCLUSIONS

This adhesive system mimics natural marine adhesives. The curing mechanisms are believed to be similar to the quinone-tanning process in nature. Because the quinone-tanning process is extremely complex, further research is warranted to fully understand the adhesion mechanisms and to pinpoint prevailing reactions occurred in the curing process. This study at

least demonstrated that the adhesion mechanisms of marine adhesives could be utilized for development of formaldehyde-free wood adhesive systems. Our results show that direct use of a polymer with a phenolic hydroxyl group as a wood adhesive could produce wood composites with high shear strengths when compared with a commercial PF glue mix for production of LVL. Although it is unlikely that PVP would be used as a wood adhesive because of its high price, the demonstration of this new concept in adhesives would likely promote further research toward developing a cost-competitive wood adhesive that works on the same principle as the one shown in this study.

ACKNOWLEDGMENT

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INVESTIGATION OF CHITOSAN-PHENOLICS SYSTEMS AS WOOD ADHESIVES

*Svetlana Peshkova and Kaichang Li**

Department of Wood Science and Engineering, Oregon State University,
Corvallis, OR 97331

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525 B Street, Suite 1900, San Diego, CA 92101-4495, US

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ABSTRACT

Chitosan–phenolics systems were investigated as wood adhesives. Adhesion between two pieces of wood veneer developed only when all three components—chitosan, a phenolic compound, and laccase—were present. For the adhesive systems containing a phenolic compound with only one phenolic hydroxyl group, adhesive strengths were highly dependent upon the chemical structures of phenolic compounds used in the system and the relative oxidation rates of the phenolic compounds by laccase. The adhesive strengths were also directly related to the viscosity of the adhesive systems. However, for the adhesive systems containing a phenolic compound with two or three phenolic hydroxyl groups adjacent to each other, no correlations among adhesive strengths, relative oxidation rates of the phenolic compounds by laccase, and viscosities were observed. The adhesion mechanisms of these chitosan–phenolics systems were proposed to be similar to those of mussel adhesive proteins.

KEYWORDS

Chitosan, laccase, phenolic compounds, marine adhesive proteins, wood adhesives, quinone-tanning.

INTRODUCTION

Wood composites are mainly made with woody materials with small dimensions (wood particles, strands, or veneer) and a wood adhesive. When compared with solid wood, wood composites have many advantages such as consistent physical properties and resistance to dimensional changes. Wood composites could also be made with woody materials of low grades and provide large panels. Therefore, wood composites have been increasingly used in construction of furniture and houses in the past 60 years.

In the production of wood composites, a wood adhesive is one of the major non-woody materials. In general, adhesive contents in wood composites are as follows: particleboard, 6–8 wt %; medium density fiberboard (MDF), 8–10 wt %; plywood, 3–5 wt %; and oriented strand board (OSB), 2–5 wt % (Haygreen and Bowyer, 1996). In 1999, the forest products industry in the United States and Canada spent over 7.4 billion dollars on wood adhesives (Johnson, 2000).

Among commercial wood adhesives, consumption of urea-formaldehyde resins (UF) holds first place, followed by phenol formaldehyde (PF) resins, and then by melamine formaldehyde (MF) resins (Meyer and Hermans, 1985). The formaldehyde-based resins, however, have a tendency to release residual formaldehyde during the manufacturing and use of wood panels. Formaldehyde vapor is potentially carcinogenic and hazardous to human health, causing eye and throat irritations as well as respiratory discomfort. At present, the occupational safety limit for released formaldehyde is about 1 ppm (Meyer and Hermans, 1985). Extensive efforts have been spent in recent years on lowering

formaldehyde emissions. As a result of modifying PF formulations, the amount of formaldehyde released in the production and use of PF-bonded wood composites has been greatly reduced. However, UF-bonded wood composites still release a harmful amount of formaldehyde (Kivistö and Jämsä, 1988).

Most commercial wood adhesives use petrochemicals as raw materials. High volatility of oil markets has caused great economic losses in the wood composites industry (Lambuth, 1989). In addition, there is a concern about long-term supply of the global oil resources. Therefore, increasing concerns about the effects of emissive formaldehyde on human health and our heavy dependence on petrochemicals have generated a need for development of formaldehyde-free wood adhesives from renewable natural resources.

Our approach for developing a new type of wood adhesives is based on the strong adhesive ability of the mussel-produced adhesive proteins. These proteins are able to form strong bonds on wet surfaces in a wide range of salinities and temperatures (Waite, 1990a; Waite et al., 1989). Unlike most commercial adhesives, these natural glues do not require either special surface preparation or elevated temperatures for strong adhesion. Therefore, mussel-produced proteins form a very appealing adhesive model for many industrial applications.

Mussel adhesive proteins have been extensively studied and characterized (Benedict and Waite, 1986; Deacon et al., 1997; Inoue et al., 1995; Marumo and Waite, 1987; Waite et al., 1985; Waite and Tanzer, 1980). One of the most salient characteristics for the mussel proteins is that they contain high amounts of 3,4-dihydroxyphenylalanine (DOPA) and

lysine (Waite, 1983; Waite, 1992; Waite et al., 1985; Waite and Tanzer, 1981). In mussel proteins, these amino acid residues with amino or phenolic functional groups react with each other by means of a phenol-oxidative enzyme to form strong adhesive bonds (Waite, 1985; Waite, 1987; Waite, 1990b). Extensive studies suggest that having certain functional groups such as amino groups and phenolic hydroxyl groups is the only requirement for water-resistant adhesion (Rzepecki and Waite, 1991; Waite, 1990b). For example, synthetic polypeptides that mimic marine adhesive proteins could be used as adhesives for aluminum, steel, and plastics (Yamamoto, 1987a; Yamamoto, 1987b; Yu and Deming, 1998). It has also been shown that a chitosan/dopamine/tyrosinase system could serve as a water-resistant adhesive for glass (Yamada et al., 2000). However, little information is available on whether a wood adhesive system can be developed using this natural adhesive as a model. In this study, we demonstrate that a chitosan-phenolics-laccase system could provide relatively strong adhesive strengths to wood composites. All three components—chitosan, a phenolic compound, and laccase—are required to create strong adhesion. The adhesive strengths are highly dependent upon the chemical structure of the phenolic compound in the adhesive system.

MATERIALS AND METHODS

Reagents. Chitosan (high molecular weight, CAS: 9012-76-4) and phenolic compounds were purchased from Aldrich (Milwaukee, WI). Laccase was a gift from Novozymes, Inc. (Davis, CA). The maple veneer was a gift from State Industry (Eugene, OR).

Enzyme assay. Laccase activity was determined through monitoring the oxidation of ABTS [2,2'-azinobis(3-ethylbenzothiazoline-6-sulfonic acid) diammonium salt] (500 μ M) at 420nm ($\epsilon_{\text{max}}=3,6 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$). The determination was done in a 50 mM sodium tartrate buffer (pH 4.5) at 30°C. One enzyme unit (U) was defined as 1.0 μ mol of product formed per minute under the assay conditions (Li et al., 1998).

Preparation of chitosan-phenolics-laccase systems. A mixture of chitosan (1.61 g) and water (100 ml) was adjusted to pH 2–3 with 1 N HCl and stirred till solids were completely dissolved. The solution was filtered, diluted with water (233 ml) (chitosan concentration: 0.48% w/w, 30 mM amino group in chitosan), and adjusted to pH 5.0 with 5 N sodium hydroxide. A phenolic compound was added to the chitosan solution and mixed. The final concentration of the phenolic compound was 10 mM. Laccase (60 U) was added to the chitosan-phenolics solution. The resulting chitosan-phenolics-laccase solution was stirred for 30 hrs at room temperature. Samples were taken from the solution at pre-determined times for wood composite production and viscosity determination. The reaction was repeated at least twice for each phenolic compound. The following solutions—chitosan alone, chitosan-laccase, DOPA-laccase, and chitosan-DOPA—were used as control adhesive systems.

Determination of viscosity. Viscosity of samples taken from the chitosan-phenolics-laccase solution was determined at predetermined times with a Brookfield viscometer (model DV II+). An S62 spindle at 60 rpm was used to measure the viscosity of low-viscous solutions containing one of the following phenolics: 4-hydroxycinnamic acid (HA), dopamine (DA), phenol, or propylgallate (PG). An S64 spindle at 60 rpm was used to measure the viscosity of high viscous solutions containing one of the following phenolics:

caffeic acid, catechol, 4-methylcatechol, 3,5-dimethoxy-4-hydroxycinnamic acid, 3,4-dihydroxyphenylalanine, or 4-hydroxy-3-methoxycinnamic acid. The viscosity was determined independently at least twice for each solution.

Evaluation of adhesive properties of chitosan-phenolics-laccase systems. Maple veneer was cut into small strips (1 mm thick x 25 mm wide x 170 mm long) with the long direction being parallel to the wood grains. Wood composite specimens bonded with a chitosan-phenolics-laccase system consisted of three veneer strips (Figure 11). , The central strip was brushed on the surfaces of its both ends along the long direction with adhesive samples taken from a chitosan-phenolics-laccase solution at pre-determined times. The surface of one end of each of the two outside strips was brushed with the adhesive samples. This adhesive-brushed area at each end was 25 mm x 25 mm. The adhesive-brushed areas of these three veneer strips were overlapped and then hot-pressed at 220° F, 150 psi for 5 minutes. The lap-shear strength of the resulting wood composite specimens was determined according to the ASTM standard method D-906 on an Instron testing machine (model TTBML, A-210) with a crosshead speed of 1 cm/min. Thirteen to twenty wood composite specimens were produced for each adhesive sample and for determination of the shear strength.

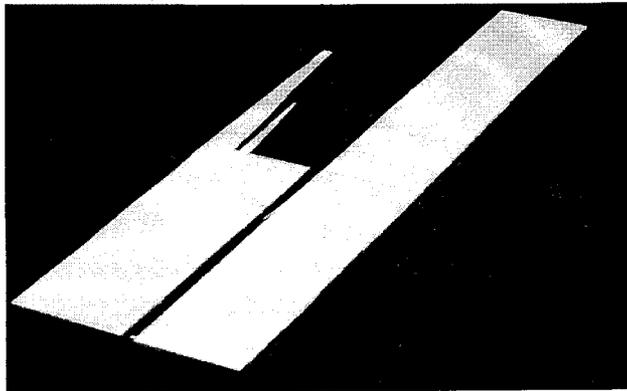


Figure 11 . A wood composites specimen (right) bonded with a chitosan-phenolics-laccase system, and the specimen after a shear-strength test (left).

Water-resistance test. The wood composite specimens prepared with the adhesive systems for the 24-hrs reaction time were soaked in tap water for 24 hrs, dried for 24 hrs in a fume hood, and then evaluated for shear strength on the Instron machine. Ten to twelve wood composite specimens for each adhesive sample were used for the water-resistance test.

Determination of oxidation rates that laccase oxidized phenolics. The wavelength of the maximum UV/visible light absorbance for a phenolic compound was determined in sodium acetate buffer (25 mM, pH 5.0) at 30°C with a UV-Vis spectrophotometer (model UV-2501PC, Shimadzu). The extinction coefficient of the phenolic compound at its maximum absorbance was determined in the same buffer at 30°C. Relative oxidation rate that laccase oxidized each phenolic compound was determined by monitoring oxidation of each phenolic compound at the wavelength of its respective maximum absorbance in sodium acetate buffer (25 mM, pH 5.0) at 30°C by using the same amount of laccase for each phenolic compound. One enzyme unit (U) was defined as 1.0 μmol of a phenolic compound consumed per minute under the assay conditions. The 100 U was set for 3,5-dimethoxy-4-hydroxycinnamic acid and used as the standard for calculation of the relative oxidation rates of the phenolic compounds by the same amount of laccase.

RESULTS

Lap-shear strengths of wood composites glued with chitosan–phenolics systems. The control adhesive systems, chitosan alone, chitosan-laccase, DOPA-laccase, and chitosan-DOPA did not offer any adhesive strength to maple veneers under the conditions studied. In other words, the wood composite specimens glued with these control adhesive systems, after hot pressing, did not hold together on cooling. However, when the three key components (chitosan, a phenolic compound, and laccase) were all present, the adhesive system yielded various shear strengths, depending on the phenolic compound used. Therefore, the chitosan-phenolics-laccase adhesive systems described in this study all contain three key components.

Chitosan-phenolics-laccase systems in which the phenolic compound contained only one phenolic hydroxyl group were first used to make the wood composites. Shear strengths of wood composites glued with a system containing 3,5-dimethoxy-4-hydroxycinnamic acid (DHA) increased with increasing reaction times, reaching maximum values at about 10 hrs (Figure 12). Shear strengths of wood composites glued with a system containing 4-hydroxy-3-methoxycinnamic acid (HMA) increased with reaction times between 1 and 6 hrs but decreased when reaction time was longer than 6 hrs. There are big variations in shear strengths for adhesive systems containing 4-hydroxycinnamic acid (HA) when reaction time was

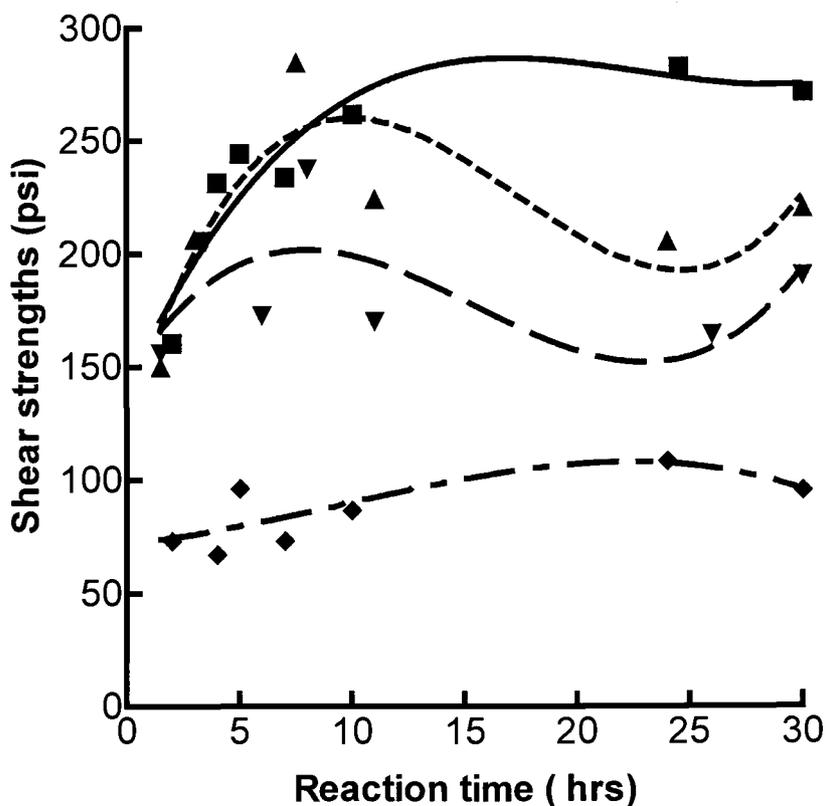


Figure 12. Shear strengths of wood composites glued with chitosan-phenolics systems containing a phenolic compound with only one phenolic hydroxyl group. The curves were obtained from nonlinear regression (polynomial: third order) of data using GraphPad's Prism program. Legend: adhesive systems containing 3,5-dimethoxy-4-hydroxycinnamic acid (■, —); adhesive systems containing 4-hydroxy-3-methoxycinnamic acid (▲, ---); adhesive systems containing 4-hydroxycinnamic acid (▼, - - -); adhesive systems containing phenol (◆, - - -).

between 1 and 10 hrs. Shear strengths for phenol were much lower than those for other phenolics. Over all, shear strengths for adhesive systems containing these four phenolic compounds are in the following order: DHA > HMA > HA > phenol.

Shear strengths of wood composites glued with adhesive systems containing a phenolic compound with two or more phenolic hydroxyl groups on the same aromatic ring are shown in Figure 13. Except for the curve for DOPA, all curves were obtained by nonlinear regression (polynomial: third order) of data using GraphPad's Prizm program. For chitosan-phenolics systems containing caffeic acid (CA), reaction times of 1 to 30 hrs appeared to have limited effects on shear strengths. Shear strengths of wood composites glued with adhesive systems containing catechol gradually increased with increasing reaction times, reaching maximum value at about 18 hrs. For adhesive systems containing DOPA, shear strengths dramatically increased between 1 hour and 2 hrs of reaction time and then flattened out. Shear strengths of wood composites glued with adhesive systems containing 4-methylcatechol (MC) increased significantly from 1 to 24 hrs of reaction time and then remained constant. Adhesive systems containing CA, catechol, DOPA, or MC had comparable shear strengths for reaction times between 18 and 26 hrs. Shear strengths of wood composites glued with adhesive systems containing propylgallate (PG) slowly increased from 1 to 12 hrs and then remain unchanged; these systems had much lower shear strengths than those containing CA,

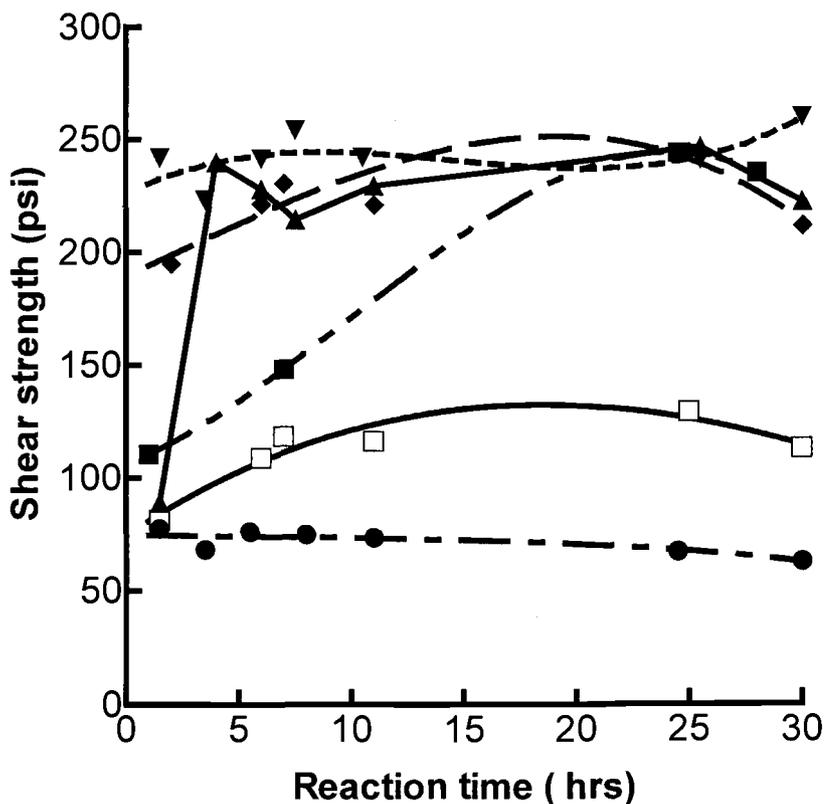
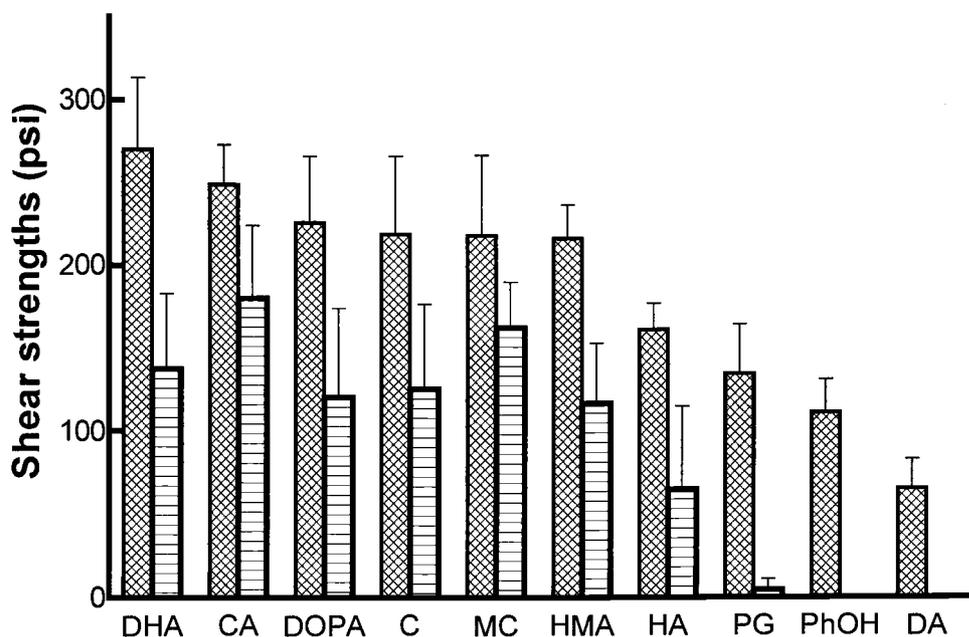


Figure 13. Shear strengths of wood composites glued with adhesive systems containing a phenolic compound with only one phenolic hydroxyl group. The curves were obtained from nonlinear regression (polynomial: third order) of data using GraphPad's Prizm program. Legend: adhesive systems containing caffeic acid (▼, ---); adhesive systems containing DOPA (▲, —); adhesive systems containing catechol (◆, - - -); adhesive systems containing 4-methylcatechol (■, - - - -); adhesive systems containing propylgallate (□, —); adhesive systems containing dopamine (●, - · - ·).

catechol, DOPA, or MC. Shear strengths of wood composites glued with a system containing dopamine were very low and were not enhanced by an increase in reaction time. Comparison of results shown in Figure 2 with those in Figure 3 reveals that adhesive systems containing DHA may have slightly higher shear strengths than those with CA, catechol, DOPA, or MC.

Water resistance. Water resistance values for wood composites glued with chitosan–phenolics–laccase systems are shown in Figure 14. Seven out of ten adhesive systems gave some level of water resistance. The retention of shear strength was highest for the wood composites glued with adhesive systems containing CA. Those with MC retained the second highest strengths after a water-soaking-and-drying (WSAD) treatment. After the WSAD treatment, shear strengths of wood composites glued with adhesive systems containing DHA, DOPA, catechol, or HMA were comparable. Complete delamination of wood composites glued with adhesive systems containing propylgallate, phenol, or dopamine was observed.

Relative oxidation rates of phenolics by laccase. Relative oxidation rates of phenolics by laccase were determined by a UV-Vis spectrophotometric method (Table). The order of oxidation rates of phenolics determined by the UV-Vis spectrophotometric method was consistent with that determined by an oxygen electrode method (data not shown) (Xu, 1996). The oxidation rate of propylgallate could not be determined with this procedure because the characteristic absorption of the oxidation products overlapped with those of propylgallate.



Phenolics in chitosan-phenolics systems

Figure 14. Shear strengths of chitosan-phenolics systems before and after a water-soaking-and-drying (WSAD) treatment. Legend: shear strengths before a WSAD treatment (\square); shear strengths after a WSAD treatment (\square). DHA, 3,5-dimethoxy-4-hydroxycinnamic acid; CA, caffeic acid; DOPA, 3,4-dihydroxylphenylalanine; C, catechol; MC, 4-methylcatechol; HMA, 4-hydroxy-3-methoxycinnamic acid; HA, 4-hydroxycinnamic acid; PG, propylgallate; PhOH, phenol; and DA, dopamine.

Table. Relative oxidation rates of phenolic compounds by laccase.

Compounds	U \pm SD*
DHA	100 \pm 7.0
HMA	95.54 \pm 4.76
Catechol	61.41 \pm 3.56
4-Methylcatechol	61.75 \pm 6.36
Caffeic acid	37.39 \pm 1.75
Dopamine	34.65 \pm 3.46
DOPA	20.07 \pm 1.16
HA	3.26 \pm 0.22
Phenol	1.85 \pm 0.09
Propylgallate	ND

* SD, standard deviation.

Viscosity of the chitosan-phenolics systems. The viscosity of the control solutions remained at 30 cPs (S62 spindle, 60 rpm) over the test period of 30 hrs. When an aqueous solution of laccase, chitosan, and a phenolic compound was stirred at room temperature, the viscosity of the solution varied greatly with the phenolic compound used. Effects of reaction time on viscosity of adhesive systems containing a phenolic compound with one phenolic hydroxyl group are shown in Figure 15. Viscosity of adhesive systems containing DHA greatly increased between 1 and 24 hrs and then decreased from 24 hrs on. With an increase in reaction time, viscosity of adhesive systems containing HMA rapidly increased, but at times of 3 to 27 hrs, viscosity was lower than for adhesive systems containing DHA. Compared with adhesive systems containing DHA or HMA, those containing HA had a much smaller increase in viscosity over a reaction time of 30 hrs. Using phenol resulted in little change in viscosity.

Effects of reaction time on viscosity of adhesive systems containing a phenolic compound with two phenolic hydroxyl groups are shown in Figure 16. It is worth noting that the scale of viscosity in Figure 16 is much higher than that in Figure 15. Catechol, CA, and MC resulted in rapid increases in viscosity over a reaction time of 30 hrs. The viscosity of an aqueous chitosan-laccase solution containing catechol dramatically increased in the first 10 hours of reaction and then increased at a slower pace from then on. Viscosity of adhesive systems containing CA also increased rapidly during the first 10 hrs, whereas for those containing MC,

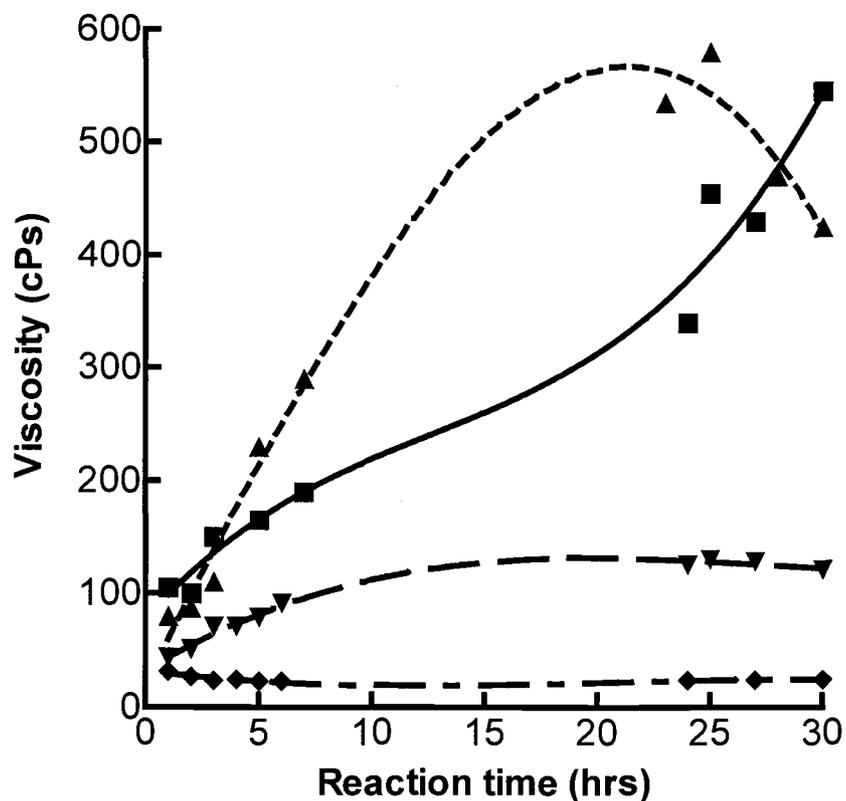


Figure 15. Viscosities of chitosan-phenolics systems containing a phenolic compound with only one phenolic hydroxyl group. Legend: adhesive systems containing 3,5-dimethoxy-4-hydroxy cinnamic acid (▲, ---); adhesive systems containing 4-hydroxy-3-methoxycinnamic acid (■, —); adhesive systems containing 4-hydroxycinnamic acid (▼, - - -); adhesive systems containing phenol (◆, - - -).

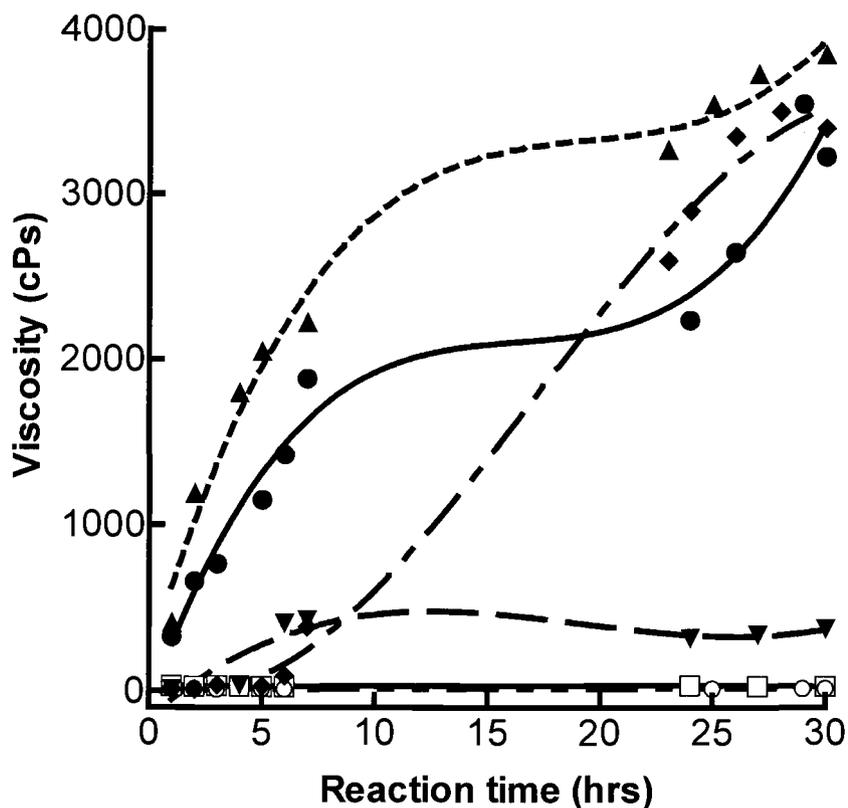


Figure 16. Viscosities of chitosan-phenolics systems containing a phenolic compound with two or three phenolic hydroxyl groups. Adhesive systems containing catechol (▲, ---); adhesive systems containing caffeic acid (●, —); adhesive systems containing 4-methylcatechol (◆, - - -); adhesive systems containing DOPA (▼, - - -); adhesive systems containing propylgallate (□, —); adhesive systems containing dopamine (○, - - -).

viscosity increased only slightly between 1 and 6 hrs and then increased rapidly. DOPA increased the viscosity slowly in the first 10 hrs and remained unchanged from 10 hrs on. There was little change in viscosity for adhesive systems containing either PG or dopamine.

DISCUSSION

The control adhesive systems including chitosan alone, chitosan-laccase, DOPA-laccase, and chitosan-DOPA had neither detectable increases in viscosity over the 30-hour reaction time nor the ability to glue maple veneers. This implies that three components—laccase, chitosan, and a phenolic compound—have to be present for providing adhesive strength to wood composites.

Laccase oxidizes a phenolic compound via a single electron oxidation to form phenolic free radicals. The phenolic free radicals can couple with each other to form dimer and even polymeric substances. Reaction of the phenolic free radicals with oxygen would form quinones. A phenolic compound could also be directly oxidized to form quinones by oxygen at an elevated temperature. In the presence of an amino compound, quinones would undergo various cross-linking reactions, a process known as quinone-tanning in nature (Waite, 1990b). We believe that a chitosan-phenolics-laccase adhesive system undergoes similar reactions in the quinone-tanning process. In fact, covalent linkages from a Michael addition reaction or Schiff base formation between the amino group in chitosan and a quinone has been proposed in a chitosan-dopamine-tyrosinase system (Yamada et al., 2000).

The chemical structure of a phenolic compound defines its oxidation rate by laccase and the tendency of the phenolic free radicals to couple with each other or to be further oxidized by oxygen to form quinones. The relative oxidation rates of phenolic compounds by laccase will definitely play an important role in the viscosity increase and the adhesive strengths of a chitosan-phenolics-laccase system. However, the correlation between relative oxidation rates and the increases in viscosity and adhesive strengths is not straightforward. If the free radicals from the oxidation of a phenolic compound by laccase tend to couple with each other, rather than to be oxidized to form quinones, the fast oxidation of the phenolic compound by laccase may not contribute much to the formation of quinones for various cross-linking reactions with chitosan. As a result, the increase in viscosity and adhesive strength may not be proportional to the increase in oxidation rates.

The increase in viscosity most probably was caused by chemical reactions between the amino group in chitosan and quinones from oxidation of a phenolic compound. Because of the possibility of the free radical coupling reactions, it is hard to predict the size of the phenolic substances attached to the chitosan backbone. These hydrophobic phenolic moieties form gel network junctions, contributing to the increase in viscosity. This high viscosity could be due to the high degree of phenolic grafting on the chitosan chain, or to the high degree of phenol coupling and low degree of grafting of bigger phenolic moieties, or to both. Therefore, viscosity readings cannot explain which reaction is predominant in each system, but they can reveal the degree of chemical alterations on the chitosan in the system. As they approached the 30-hour reaction time, some of the adhesive systems demonstrated a plateau in viscosity levels or even a

decrease. An observed decline in viscosity could be explained by the reversible nature of Schiff bases in water (Kumar et al., 2000).

For chitosan-phenolics-laccase systems containing a phenolic compound with only one phenolic hydroxyl group, the oxidation rates, the viscosity increase, and the shear strengths each have the same order: DHA>HMA>HA>phenol. In other words, the faster a phenolic compound is oxidized by laccase, the quicker the increase in the viscosity, and the greater the shear strength. The oxidation rate of a phenolic compound is dependent upon the difference between the redox potential of the phenolic compound and that of the laccase. With the same laccase, the lower the redox potential of the phenolic, the faster the oxidation. A methoxy group is an electron-donating group. A methoxy-substituent on a phenolic compound would lower the redox potential, thus increasing the oxidation rate. Therefore, the oxidation rates for phenolic compounds with only one phenolic hydroxyl group are consistent with the number of methoxy groups.

For adhesive systems containing a phenolic compound with two or three phenolic hydroxyl groups adjacent to each other, there is a very different relationship between oxidation rates and viscosity and shear strength. Regardless of oxidation rates and viscosity values, most of these adhesive systems—except those containing PG and DA—demonstrated similar adhesive strengths (200–250 psi). Laccase oxidized these compounds at a much slower rate than it oxidized DHA and HMA. However, the adhesive systems containing CA, DOPA, catechol, and 4-methylcatechol had much higher viscosities at most reaction times than those containing DHA and HMA (please note the different Y axis scales in Figures 15 and 16). Two adjacent phenolic hydroxyl groups can form

stronger hydrogen bonds than a single phenolic hydroxyl group, which could be one of the explanations for the high viscosities of the adhesive systems containing a phenolic compound with two phenolic hydroxyl groups. It is perplexing that the adhesive system containing PG had only a small viscosity increase and low adhesive strengths. In contrast to the significant viscosity increase and the adhesive strength of a chitosan-dopamine-tyrosinase system (Yamada et al., 2000), a chitosan-dopamine-laccase system showed little change in viscosity over the 30 hrs of reaction time and provided little adhesive strength. From Table 1, we can see that dopamine was oxidized at a relatively moderate rate. Because dopamine contains both phenolic hydroxyl groups and an amino group, quinones from the oxidation of dopamine could react with this amino group (Jimenez et al., 1984). The lack of viscosity change and the shear strength suggest that reactions between dopamine and its oxidation products, rather than reactions between chitosan and oxidized products of dopamine, prevailed in the chitosan-dopamine-laccase system.

The water-resistance test revealed that at least 50% of the adhesive strength could be retained by the seven out of ten adhesive systems that received a WSAD treatment. The water-resistance results were not correlated with the oxidation rates, viscosity change, or the dry shear strengths of the adhesive systems. Since the chemistry of these adhesive systems is complex, further research is warranted to gain a better understanding of the properties of these adhesive systems.

CONCLUSIONS

A chitosan-phenolics-laccase system could be used as a wood adhesive. Chitosan, a phenolic compound, and laccase are essential components in this adhesive system. For adhesive systems containing a phenolic compound with only one phenolic hydroxyl group, adhesive strengths depend on the chemical structure of the phenolic compound. For the systems containing a phenolic compound with one phenolic hydroxyl group, adhesive strengths were closely related to the viscosity increase and the relative oxidation rates of the phenolic compound in the system. However, the adhesive systems containing a phenolic compound (except dopamine) with two phenolic hydroxyl groups adjacent to each other developed adhesive strengths comparable to each other. In other words, the chemical structures of these phenolic compounds had limited effects on shear strengths and viscosity. There was also no relationship between adhesive strengths and viscosity or the relative oxidation rates of these phenolic compounds.

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GENERAL CONCLUSIONS

This study revealed that poly (4-vinylphenol) (PVP), a commercially available polymer containing phenolic hydroxyl groups, could bond wood veneers strongly. The pendant phenolic hydroxyl groups in PVP play an essential role in the adhesion. When a substance with an amino group is used with the PVP for gluing wood, strengths of wood composites bonded with this adhesive system were much stronger than those with the PVP alone. The free-radical coupling, Michael addition reactions, and Schiff-base formation reactions were proposed to play an important role in the curing of the adhesive system. The shear strength of wood composites bonded with PVP/1,6-hexanediamine system (the 3:1 molar ratio between phenolic hydroxyl group in PVP and 1,6-hexanediamine) was comparable to that of wood composites bonded with commercial PF resins at the similar conditions.

Chitosan, a natural polysaccharide carrying amino groups, could also be used to develop a wood adhesive. In addition to chitosan, a phenolic compound and laccase are required for the chitosan-based adhesive system to bond wood. The chemical structure of the phenolic compound and the number of the phenolic hydroxyl groups greatly affect the strength and water resistance of wood composites bonded with the chitosan-phenolics-laccase adhesive systems. The adhesive strengths of the systems containing compounds with one phenolic hydroxyl group was directly related to the oxidation rate of the phenolic compounds by laccase and the system's viscosity.

Adhesion mechanisms of a PVP/amine adhesive system and a chitosan-phenolics-laccase adhesive system are similar to those of marine

adhesive protein. The curing mechanisms for these two adhesive systems are similar to the quinone-tanning process in nature. In this study, we demonstrated that the chemistry of the marine adhesive protein could be applied to development of formaldehyde-free wood adhesives. We further demonstrated that functional groups, rather than the polymer backbone play an important role in the adhesion. Our results reveal that a polymer other than proteins or polypeptides could be employed to develop a wood adhesive system, as long as the polymer contains either phenolic hydroxyl groups or amino groups. Our findings in this study would likely facilitate development of cost-competitive formaldehyde-free wood adhesive from renewable resources.

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