INVESTIGATION OF POLY(4-VINYLPHENOL) AS A WOOD ADHESIVE

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ABSTRACT

An increasing concern about the effect of emissive VOC (volatile organic compounds), 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 made up primarily 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.

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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 composed predominately 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, 1982a, b, c, Yamamoto 1987a, b, 1989a, b, 1996; Yamamoto et al. 1996; Yu and Deming 1998). These extensive studies have revealed that "functionality, and not amino acid sequence, as 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-vinylphenol can bond maple veneers very strongly in the presence of 1,6-hexanediamine.

EXPERIMENTAL

Materials

Poly(4-vinylphenol) (PVP) (an average M_w, 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 2,500 mm long, 1,270 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 diammonium salt] (500 μM) at 420 nm (ε_{max} = 3.6 × 10^4 M^{-1} 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, ΔH = 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 first 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 first 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 H_2O), stirred for 5 min at room temperature, and then used for bonding maple veneers. The repeating unit (C_8H_8O, 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 H_2O), 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 mm^2 (5 mm × 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.

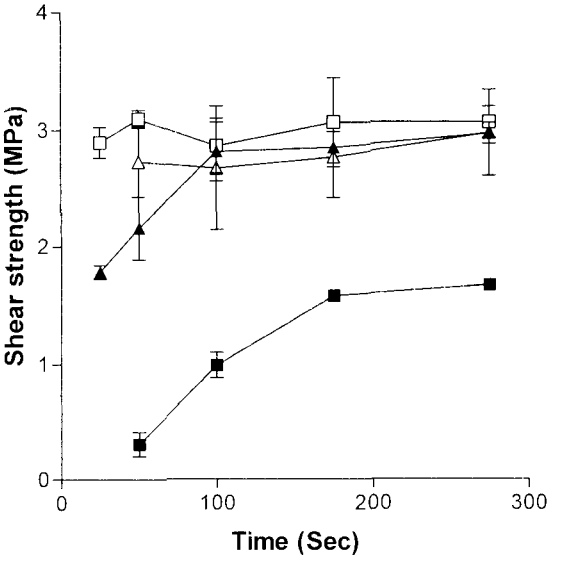


FIG. 1. Shear strengths of maple composites bonded with a PVP suspension (400 mg/ml H_2O) at various press temperatures and press times. 80°C (■), 100°C (▲), 120°C (□), and 150°C (△). Data are the means of six replicates, and the error bar represents the standard deviation.

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 Fig. 1. 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 s.

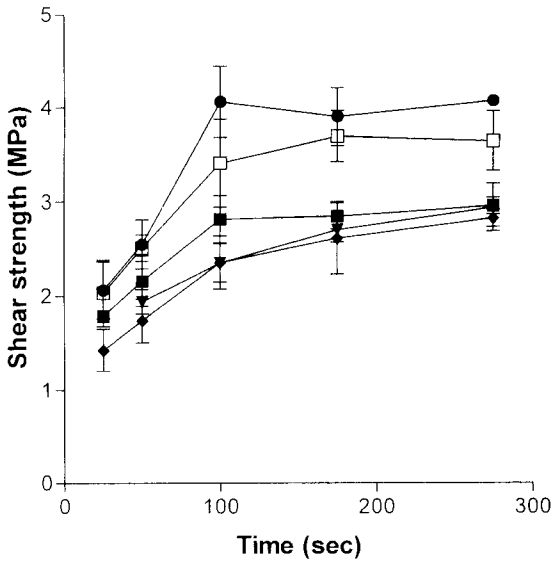


FIG. 2. Shear strengths of maple composites bonded with a PVP suspension (400 mg/ml H_2O) in the presence of various additives at the press temperature 100°C. PVP (■), PVP + O_2 (▼), PVP + laccase (♦), PVP + HDA (the molar ratio of PhOH in PVP vs. HDA, 6:1) (●), and PVP + DETA (the molar ratio of PhOH in PVP vs. DETA, 6:1) (□). Data are the means of six replicates, and the error bar represents the standard deviation.

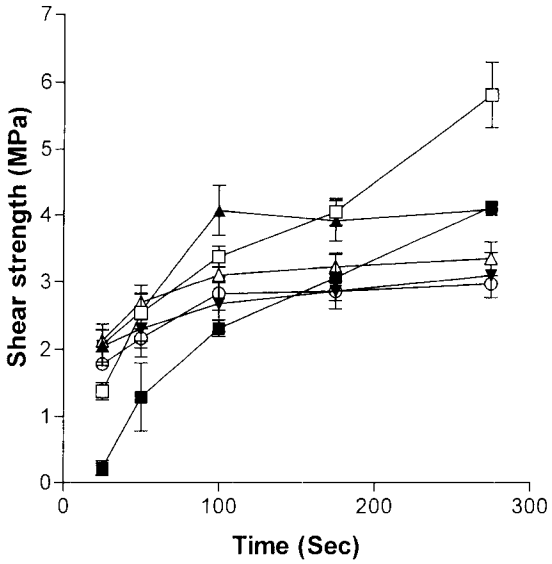


FIG. 3. The effect of molar ratios between PhOH in PVP and HDA on shear strengths at press temperature 100°C. 2:1 (■), 3:1 (□), 6:1 (▲), 9:1 (△), 12:1 (▼), and PVP without HDA (○). Data are the means of six replicates, and the error bar represents the standard deviation.

Various additives were added to the PVP suspension, and their influences on shear strengths are shown in Fig. 2. When press time was shorter than 275 s, adding a phenoloxidase laccase to the PVP suspension and bubbling O_2 in the PVP suspension each resulted in slightly lower shear strengths than that of the PVP suspension itself. When press time was 275 s, adding laccase or bubbling O_2 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 that of composites made with the PVP suspension alone. Adding HDA 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 Fig. 3, 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 s, whereas a ratio of 3:1 resulted in much higher shear strengths than any other ratios at a press time of 275 S.

Figure 4 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 s) 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 (Figs. 4 and 5). 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 (Fig. 5). At all 100°C, shear strengths increased gradually with press time. At 120°C, shear strengths increased sharply at press times of 25 to 100 s and then flattened out from 100 S. 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 s.

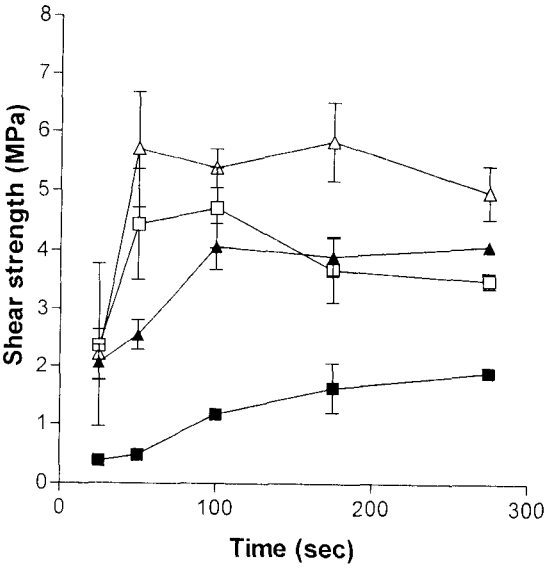


FIG. 4. Shear strengths of maple composites bonded with a PVP suspension (400 mg/ml H_2O) in the presence of HDA with a 6:1 molar ratio of PhOH in PVP vs. HDA. 80°C (■), 100°C (▲), 120°C (□), and 150°C (△). Data are the means of six replicates, and the error bar represents the standard deviation.

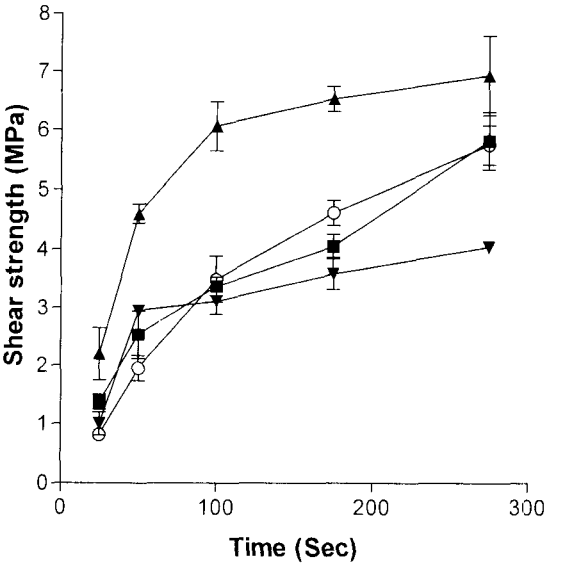


FIG. 5. Shear strengths of maple composites bonded with a PVP suspension (400 mg/ml H_2O) in the presence of HDA with a 3:1 molar ratio of PhOH in PVP vs. HDA and with a phenol-formaldehyde glue mix for LVL. 100°C (■), 120°C (▲), 150°C (▼), PF glue mix at 105°C (○). Data are the means of six replicates, and the error bar represents the standard deviation.

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 (Fig. 5). Shear strengths of the maple composites bonded with a mixture of PVP and HDA at 100°C were comparable with those bonded with the commercial PF glue mix at 105°C (Fig. 5). 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 (Fig. 5).

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 believe that PVP should be able to bond wood veneers as PF resins do. From Fig. 1, 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 cross-linking 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 cross-linking of PVP, thus resulting in lower shear strengths. When the PVP suspension is saturated with

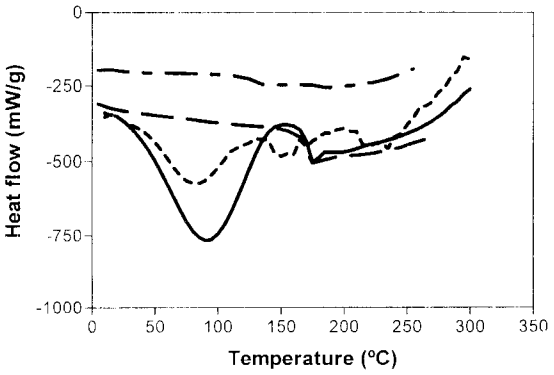
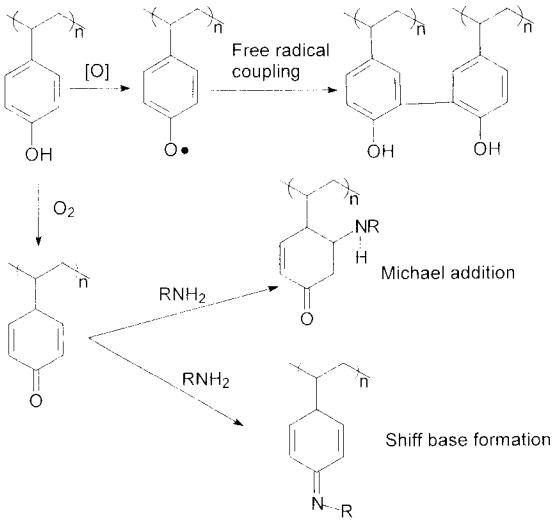


FIG. 6. DSC characterization of PVP and PVP in the presence of HDA (the 3:1 molar ratio of PhOH in PVP vs. HDA). The 1st run of PVP (———), the 2nd run of the 1st-run-PVP (— — —), the 1st run of PVP + HAD (– – –), the 2nd run of the 1st-run-(PVP+HDA) (—·—).



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

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 (Fig. 2). If the press time is sufficiently long, with the oxygen concentration being reduced, the cross-linking reactions might gradually prevail. This accounts for the comparable shear strengths for the PVP suspension and the O_2-saturated PVP suspension at a press time of 300 s. 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 (Fig. 2).

DSC spectra indeed indicate that some reactions occurred when PVP was heated (Fig. 6). 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 (Fig. 1). When the PVP sample was heated a second time, 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 (Tg) of about 150°C for the PVP used in this study. If the Tg 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 Tg at about 150°C. Moreover, visual inspection of the glueline 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 Fig. 1.

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 of Shiff 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 (Fig. 6). However, the heat absorption peak disappeared when the preheated mixture of PVP and HDA was heated again (Fig. 6), which implies the occur-

rence 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 mechanism 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.

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REFERENCES

BAUMANN, M. G. D., L. F. LORENZ, S. A. BATTERMAN, AND G.-Z. ZHANG. 2000. Aldehyde emission from particleboard and medium density fiberboard products. Forest Prod. J. 50(9):75–82.

HENDERSON, J. T. 1979. Volatile emissions from the curing of phenolic resins. Tappi J. 62:9396.

HUMPHREY, P. E. 1999. The bonding speed of adhesives: An automated evaluation system. The 33rd International Particleboard/Composite Materials Symposium, Washington State University, Pullman, WA. Pp. 139–146.

LI, K., R. F. HELM, AND K.-E. L. ERIKSSON. 1998. Mechanistic studies of the oxidation of a non-phenolic lignin model compound by the laccase/1-hydroxybenzotriazole redox system. Biotechnol. Appl. Biochem. 27:239–243.

LINDNER, E. 1984. The attachment of macrofouling invertebrates: Pages 183–201 *in* J. D. Castlow and R. C. Tipper, eds. Marine biodeterioration: An interdisciplinary study. Naval Institute Press, Annapolis, MD.

———, AND C. A. DOOLEY. 1976. Studies of the reaction mechanism of the adhesive of barnacles: Pages 333–344 *in* 4th International Congress on Marine Corrosion and Fouling. Antibes, France.

MARUTZKY, R. 1989. Release of formaldehyde by wood products. Vol 2:307–387. *In* A. Pizzi, ed. Wood adhesives—chemistry and technology. Marcel Dekker, Inc., New York, NY.

MEYER, B., B. A. K. ANDREWS, AND R. M. REINHARDT, EDS. 1986. Formaldehyde release from wood products. ACS Symposium Series 316. American Chemical Society, Washington, DC.

QIN, X. X., K. J. COYNE, AND J. H. WAITE. 1997. Tough tendons. Mussel byssus has collagen with silk-like domains. J. Biol. Chem. 272(51):32623-32627.

RZEPECKI, L. M., AND J. H. WAITE. 1991. DOPA proteins: Versatile varnishes and adhesives from marine fauna. Vol 4:119–148. *In* P. J. Scheuer, eds., Bioorganic marine chemistry. Springer-Verlag, Berlin, Germany.

———, K. M. HANSEN, AND J. H. WAITE. 1992. Characterization of a cystine-rich polyphenolic protein family from the blue mussel *Mytilus edulis* L. Biol. Bull. 183: 123–137.

WAITE, J. H. 1983. Evidence for a repeating 3,4-dihydroxyphenylalanine- and hydroxyproline-containing decapeptide in the adhesive protein of the mussel, *Mytilus edulis* L. J. Biol. Chem. 258(5):2911–2915.

———. 1985. Catechol oxidase in the byssus of the common mussel, *Mytilus edulis* L. J. Mar. Biol. Ass. U.K. 65:359–371.

———. 1987. Nature's underwater adhesive specialist. Int. J. Adhesion Adhesives 7:9–14.

———. 1990. The phylogeny and chemical diversity of

quinone-tanned glues and varnishes. Comp. Biochem. Physiol. [B] 97(1):19–29.

YAMAMOTO, H. 1987a. Adhesive studies of synthetic polypeptides: A model for marine adhesive proteins. J. Adhes. Sci. Technol. 1(2):177–183.

———. 1987b. Synthesis and adhesive studies of marine polypeptides. J. Chem. Soc., Perkin Trans. 1:613–618.

———. 1989a. Adhesive proteins. Nippon Setchaku Kyokaishi 25(5):187–193.

———. 1989b. Water system adhesion of hydrophilic proteins. Hyomen 27(10):810–820.

———. 1996. Marine adhesive proteins and some biotechnological applications. Vol. 13:133–165. *In* M. P. Tombs, ed. Biotechnology and genetic engineering reviews. Intercept, Andover, England.

———, AND T. HAYAKAWA. 1979. Synthesis of sequential polypeptides containing L-β-3,4-dihydroxyphenyl-α-alanine (DOPA) and L-glutamic acid. Biopolymers 18(12):3067–3076.

———, AND ———. 1982a. Catalytic actions of synthetic polypeptides: 2. Stereoselective inhibition of ascorbic acid oxidation by the basic polypeptide-copper(II) complexes. Int. J. Biol. Macromol. 4(2):116–120.

———, AND ———. 1982b. Conformational studies of sequential polypeptides containing L-.beta.-3,4-dihydroxyphenyl-.alpha.-alanine (DOPA) and L-glutamic acid. Int. J. Biol. Macromol. 4(5):258–62.

———, AND ———. 1982c. Synthesis of sequential polypeptides containing L-β-(3,4-dihydroxyphenyl)-α-alanine (DOPA) and L-lysine. Biopolymers 21(6):1137-1151.

———, M. ASAI, H. TATEHATA, AND K. OHKAWA. 1996. Structures, synthesis and surface characteristics of marine adhesive proteins. Pept. Chem. 33rd:349–352.

YU, M., AND T. J. DEMING. 1998. Synthetic polypeptide mimics of marine adhesives. Macromol. 31(15):4739–4745.