Condensed tannin-resorcinol adducts in laminating adhesives

Roland E. Kreibich
Richard W. Hemingway

Abstract

A condensed tannin-resorcinol adduct made by coreaction of an extract from southern pine bark with resorcinol at a 2 to 1 weight ratio was used to prepare a laminating resin in which the entire amount of resorcinol normally used was replaced by this adduct. The resin was formulated into a room temperature setting adhesive that meets the basic criteria of product standards governing approval by the American Institute of Timber Construction.

In efforts to find uses for bark that would provide returns exceeding fuel values and to reduce the forest products industry dependence on chemical producers, there has been a long history of research directed to the use of conifer bark extracts in wood adhesives (1). Successful commercial development of wattle tannin-based adhesives (9) has spurred on efforts to develop similar products based on conifer bark extracts despite the fact that the chemistries of these two types of tannins are quite different.

Although the scientific literature is extensive (1, 9), there have been few commercial successes in the use of conifer bark extracts. These tannins are noted for their extremely high aldehyde reactivity; because of this, and the high cost of resorcinol, it seems that successful applications of conifer bark tannins would be more likely in the development of cold setting laminating adhesives. Condensed tannins from wattle (10, 11) and western hemlock (7) barks have been successfully incorporated into wood laminating adhesives.

The condensed tannins in southern pine barks are predominantly procyanidin polymers of a comparatively broad molecular weight distribution centering on 2,000 to 3,500 (i.e., 7 to 12 flavonoid units) as a number average (2, 3, 8, 12). If the molecular weight of these tannins could be reduced, and if these products were used similar to resorcinol as the reactive center of a phenol-resorcinol-formaldehyde resin, these products could have potential in laminating adhesives. Our initial efforts toward this objective have been described (4).

To summarize, it was considered that useful low molecular weight tannin-resorcinol adducts might be obtained through an acid-catalyzed cleavage and condensation of procyanidins with resorcinol. It was known that the interflavonoid bond of procyanidin-based tannins was particularly labile to acid-catalyzed cleavage (6), while that of a flavan-4-resorcinol adduct was expected to be much more stable. Therefore, in a reaction of tannin with resorcinol under acidic conditions, a thermodynamic equilibrium could favor the formation of the flavan-4-resorcinol adduct despite the much higher nucleophilicity of the phloroglucinol *A*-ring of the tannin as compared with resorcinol. This hypothesis was verified, and although the yields of flavan-4-resorcinol adducts were low, comparatively high yields of low molecular weight oligomeric procyanidin-4-resorcinol adducts were obtained from a reaction of a crude tannin extract from southern pine bark (2 parts) with resorcinol (1 part) with acetic acid catalyst at 120°C (4).

This Product-A was used in place of the resorcinol in a conventional cold setting laminating adhesive. Product-A showed good reactivity during the resin preparation. During the final step of resin advancement, the control resin made with resorcinol needed to be kept under reflux for 4 to 5 hours in order to advance to the desired viscosity. In the experimental resin where all the resorcinol had been replaced by Product-A, this reflux time had to be shortened to about 2 hours to achieve resins with (what was judged to be) suitable viscosity. Such Product-A derived resins did yield mediocre glueline durability values as compared to their resorcinol counterparts.

Microscopic examination of the tannin-resorcinol adducts and resins prepared from them showed that

---

The authors are, respectively, Consultant, 4201 South 344th St., Auburn, WA 98001; and Project Leader, Forest Products Utilization Research, Southern Forest Expt. Sta., USDA Forest Serv., 2500 Shreveport Highway, Pineville, LA 71360.
This paper was received for publication in April 1984.

Forest Prod. J. 35(3):23-25.

these were not completely soluble in water and that small insoluble particles were present. Chemical analysis of the product of reaction of the crude tannin with resorcinol disclosed that it contained approximately 20 percent of carbohydrates. This crude product could be purified of carbohydrates by extraction into ethyl acetate from water with no significant loss of phenolics (4). Because of the large difference in estimated production costs for extracts from southern pine bark of about \$0.16/lb. (5) and purchase costs of resorcinol of about \$1.75/lb., it was considered that this process should still be feasible even with an additional purification step as a requirement. The work described here, therefore, evaluates the use of a purified condensed tannin-resorcinol adduct (Product-B) in room temperature to cure wood laminating adhesives. For more detailed information of the chemistry of the Products-A and -B, consult Hemingway and Kreibich (4).

Experimental

Prepolymer — A phenol-formaldehyde prepolymer was made by reacting one mole of phenol with one mole of formaldehyde in the presence of 6.6 percent of sodium hydroxide based on the weight of phenol. Water, 64.2 percent based on the weight of the phenol, was present as a diluent. The reaction mixture was heated under reflux to a viscosity of 160 centipoise.

Resin VI — The prepolymer (51.84 g) was combined with Product-B (16 g) and water (8.9 g) was added. This mixture was heated in a steam bath (98° to 99°C) with occasional stirring for 1.5 hours. The resin was cooled and ethanol (3.2 g) was added. The Gardner-Holdt viscosity of this resin was B-C.

Adhesive VI — Walnut shell flour (1.0 g), paraformaldehyde (0.20 g), and 50 percent formalin (3.0 g) were blended with the resin VI (10.0 g). The viscosity of this mixture was still too low, so a high water requirement attapulgite clay and wood flour were added in sufficient quantity to achieve what was considered an appropriate adhesive viscosity.

Resin VII — After an aliquot (10.0 g) had been removed from Resin VI (for the purpose of preparing adhesive VI), the remainder was quickly heated on a hot plate and then kept in a steam bath at 94°C for 1 hour. At the end of this reaction, the cooled resin had a Gardner-Holdt viscosity in the Z-range (too dark to measure accurately).

Adhesive VII — The Resin VII (10.3 g) was combined with walnut shell flour (1.4 g), paraformaldehyde (0.20 g), and 50 percent formalin (3.4 g).

Resin VIII — For Resin VIII the formaldehyde/phenol molar ratio of the prepolymer was left at 1.0; the water was reduced to 56.5 percent, the sodium hydroxide to 6.0 percent, based on the phenol.

The prepolymer (51.84 g) was combined with Product-B (16.0 g) and water (9.0 g). The mixture was stirred at ambient temperature for 18 hours in an attempt to break up all small lumps, but this was not completely successful. The mixture was then heated in a steam bath (98° to 99°C) for 2 hours and 10 minutes with intermittent (2 to 3 min.) removal for intermittent stirring where the temperature fell to 92° to 95°C. After cooling to 50°, isopropanol (4 mL) was added and the mixture was allowed to cool to room temperature.

Adhesive VIII — This Resin VIII (20.1 g) was combined with walnut shell flour (2.8 g), paraformaldehyde (0.47 g), and 50 percent formalin (7.3 g).

Gelation studies — Small samples (about 1 g) of the Resins VII and VIII were combined with paraformaldehyde and/or 50 percent formalin at various levels (ratios) and the gel times at room temperature and the quality of the resulting gels were observed. In the cases where gels appeared to have good characteristics, about one-half of the finally cured resin was suspended in water, the other half in a mixture of water and isopropanol (50/50), allowed to stand for 1 week, then boiled briefly in order to observe coloring of the solvents and thus obtain qualitative information about the solubility (and therefore degree of cure) of these polymers.

Gluing studies — Each of the above adhesives was applied to random grain Douglas-fir panels (3/4 in. by 6 in. by 8 in.) at film (not bead) spread rates of 70 to 80 lb./1000 ft.^{2} of single glueline; one panel (with Adhesive VIII) was spread at a rate of only 40 lb./1000 ft.^{2}. After closed assembly times of 5 to 10 minutes, the panels were pressed at 72°F for at least 16 hours. Six shear specimens (PS 56-73) were prepared from each panel, and of the six, two specimens were sheared dry (ASTM 107), two were sheared after cyclic vacuum pressure water soak (AITC 110), and two were submerged for 2 hours in boiling water and sheared wet.

Results and discussion

It should be emphasized at the outset that at the present stage of this work, only small quantities of resin and adhesive could be prepared, so a thorough evaluation of this approach to a laminating adhesive has not yet been possible. Such an evaluation must employ a number of different hardener concentrations and compositions, a number of assembly times, several spread levels and, often most critical, widely different viscosities of the resin and of the adhesive. The up-to-date results do show, however, that a purified condensed tannin-resorcinol adduct (Product-B) is capable of totally replacing the resorcinol in a laminating resin and such a resin, with proper formulation as an adhesive, will yield room temperature cure gluelines meeting the basic criteria of the Product Standards.

The results of the gelation studies showed that these resins made with the condensed tannin-resorcinol adducts, when blended with excess formaldehyde, gelled similar to a typical phenol-resorcinol-formaldehyde laminating resin (Table 1).

The rate of gelation was not so rapid as to prohibit satisfactory adhesive mixing and application. The gelation rate and quality of the gel varied significantly with the hardener used. The cured resins were not soluble in room temperature or boiling water or a mixture of 50 percent water and 50 percent isopropanol. More work may have to be done to extend the working life of such adhesives. Resin VI was not advanced very far in comparison with VII and VIII, yet gluebond quality was not

TABLE 1. *Gelation properties of tannin-resorcinol adduct resins.*

	Resin VII				Resin VIII			
	A	B	C	D	K	L	M	N
Resin (g)								
Paraform (g)								
Formalin (g)								
Time at 20°C								
35 min.	liq.	liq.	liq.	liq.	liq.	liq.	liq.	liq.
	start gel	start gel	high visc.	start gel	high visc.	high visc.	high visc.	high visc.
135 min.	poor gel	hard gel	hard gel	hard gel	high visc.	hard gel	hard gel	poor gel

ªBecause of small quantities of materials available, conventional gel time methods could not be used.

drastically affected. Therefore, good opportunities exist to extend the working life of the adhesive through modification of the resin synthesis and adhesive formulation.

It is well known that the rate of gelation and the speed of hardening of such adhesives can be greatly influenced by the variation of the pH of the system. Experimentation with adjusting the pH over a given range in order to determine the gel time or cure time response to such change was not done, again due to the up-to-date limited availability of raw material. It should be mentioned here, however, that all resins and adhesive mixes prepared had a pH between 7.5 and 9.0. Variation of this pH will provide another means to tailor the system for specific manufacturing requirements.

The gluebond quality of specimens made with glues VII and VIII at spread rates of 70 lb./1000 ft.^{2} generally meets the criteria of shear strength and wood failure in dry shear, cyclic vacuum pressure water soak, and 2-hour boil tests (Table 2).

A reduction of the glue spread rate from 70 to 40 lb./1000 ft.^{2} (Adhesive VIII) did drop the gluebond quality far below Product Standard criteria for the cyclic vacuum pressure water soak test, but the dry shear and 2-hour boil tests were satisfactory. The high shear strength of the vacuum pressure samples probably contributed to the low wood failure readings. This and the fact that the wood failures of AITC 110 tests have been improved from the initial range of zero to 18 percent in our earlier work (4) to the present levels with the formulation of only a few adhesives made from Product-B certainly provide reasons for optimism. Additional work required to more fully evaluate these resins is in process.

TABLE 2. — *Gluebond quality from tannin-resorcinol adduct resins.*ª

Adhesive spread rate	VI 70 lb.	VII 70 lb.	VIII 70 lb.	VIII 40 lb.
Dry shear (AITC 107)				
Shear strength (psi)	1680	1890	1800	1600
Wood failure (%)	62	82	92	97
Vacuum pressure (AITC 110)				
Shear strength (psi)	510	610	780	1020
Wood failure (%)	52	88	70	35
2-hour boil				
Shear strength (psi)	990	780	1020	1060
Wood failure (%)	88	95	87	72

ªAll values are averages of two specimens only.

Significance

Current commercial PRF laminating adhesive resins contain about 16 to 18 percent resorcinol. Through the chemistry and process we have described here, the content of resorcinol added as a chemical was lowered to about 6-1/2 percent, based on liquid resin.

It must be kept in mind, however, that this has been achieved with added costs for the isolation and derivatization of the tannin component.

Conclusions

Over 60 percent of the resorcinol requirement in a room temperature cure wood laminating adhesive can be replaced by extracts from southern pine bark through use of a condensed tannin-resorcinol adduct. These adhesives show promise to meet the basic criteria of the U.S. Product Standards.

Literature cited

1. Hemingway, R.W. 1981. Bark: its chemistry and prospects for chemical utilization. *In* I.S. Goldstein, (ed.) Organic Chemicals From Biomass, CRC Press Boca Raton, Fla., pp. 190-248.
2. ________, L.Y. Foo, and L.J. Porter. 1982. Linkage isomerism in trimeric and polymeric 2,3-*cis* procyanidins. J. Chem. Soc. Perkin Trans. I. 1209-1216.
3. ________, J.J. Karchesy, G.W. McGraw, and R.A. Wielesek. 1983. Heterogeneity of interflavonoid bond location in loblolly pine bark procyanidins. Phytochemistry 22(1): 275-281.
4. ________ and R.E. Kreibich. Condensed tannin-resorcinol adducts and their use in wood-laminating adhesives: an exploratory study. J. Applied Polymer Sci. (in press).
5. ________ and R.C. Lloyd. 1982. Economic prospects for conifer bark extracts. USDA-FS, Final Rep. FS-SO-3201-47.
6. ________ and G.W. McGraw. 1983. Kinetics of acid-catalyzed cleavage of procyanidins. J. Wood Chem. and Techn. 3(4):421-435.
7. Herrick, F.W., and R.J. Conca. 1960. The use of bark extracts in cold setting water proof adhesives. Forest Prod. J. 10(7):361-368.
8. Karchesy, J.J., and R.W. Hemingway. 1980. Loblolly pine bark polyflavonoids. J. Agric. Food Chem. 28(2):222-228.
9. Pizzi, A. 1980. Tannin-based adhesives. J. Macromolecular Sci., Rev. in Macromolecular Chem. C 18(2): 247-315.
10. ________ and F.A. Cameron. Fast setting phenolic adhesives for gluelam timber taken to their limits. J. Applied Polym. Sci. (in press).
11. ________ and G.M.E. Daling. 1980. Laminating wood adhesives by generation of resorcinol from tannin extracts. J. Applied Polym. Sci. 25:1039-1048.
12. Williams, V.M., L.J. Porter, and R.W. Hemingway. 1983. Molecular weight profiles of proanthocyanidin polymers. Phytochemistry 22(2): 569-572.