The Chemistry and Development of Tannin-Based Adhesives for Exterior Plywood

A. PIZZI and H. O. SCHARFETTER, *National Timber Research Institute, South African Council for Scientific and Industrial Research, Pretoria, Republic of South Africa*

Synopsis

Condensed tannins are phenolic in nature and undergo reaction with formaldehyde to form resins. Tannin/formaldehyde condensates tend to have a low degree of condensation resulting in bonds lacking strength and water resistance. Small amounts of short-length phenol/resorcinol/formaldehyde, phenol/formaldehyde, and urea/formaldehyde polymers are used to increase the degree of polymerization of tannin-formaldehyde resins, decreasing brittleness and increasing water resistance. Furfural is used to plasticize tannin/formaldehyde resins to improve the distribution of stress forces on the glueline, overcoming weakness due to stress concentration. Exterior plywood panels were prepared using these modified tannin/formaldehyde resins as adhesives. The modified tannin/formaldehyde adhesives perform well, have similar characteristics to and are as easy to use as phenol/formaldehyde adhesives, and also have a few advantages, especially tolerance to faster pressing times.

INTRODUCTION

Tannin-based wood adhesives made by the base-catalyzed polymerization of condensed tannins with formaldehyde have been described as substitutes for synthetic phenolic resins by different authors.[1-3,5,8-10,14] The tannin of the black wattle tree (*Acacia mearnsii*), easily available on commercial scale, was used.

Most tannin-adhesive resins previously reported had serious disadvantages such as poor strength, poor adhesion, brittleness, impractical shelf- and potlives, long pressing times, short assembly times, or uneconomical conditions of application. These disadvantages have severely limited the industrial use of these resins.

The disadvantages listed above were thought to be due to some of the following causes: (1) High reactivity of the tannin resulting in a short potlife; (2) weakness of tannin/formaldehyde condensates due to limited crosslinking; (3) the disregard shown by previous authors of realistic industrial conditions. This paper describes new approaches to these problems and shows that the formation of resins with physical properties, chemical durability, and ease of use comparable to those of commercial phenolic resins is possible.

The approach adopted in improving the strength properties was to increase crosslinking by employing reagents with longer molecules because the methylene bridges formed by formaldehyde were considered too short to bridge over longer distances as those found in the case of bulky tannin molecules. Another factor that might reduce the effectiveness of formaldehyde as hardener is the immo-

bilization of the tannin molecules by the first methylene bridges formed so that large distances between reactive points preclude any further crosslinking by short methylene bridges.

IMPROVEMENT OF DEGREE OF CONDENSATION

The structure of the main polymeric constituent of wattle tannin may be represented as follows[11,12]:
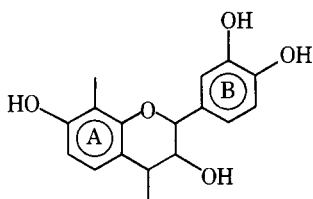
This flavonoid unit is repeated 2–11 times, and the different units are linked as follows[11,12]:
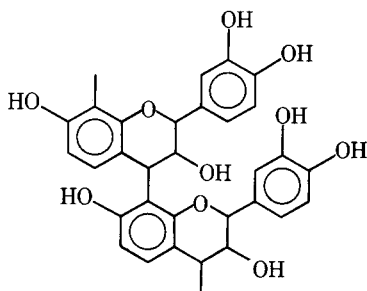
The nucleophilic centers on the A ring of a flavonoid unit tend to be more reactive than those found on the B ring. This is due to the vicinal hydroxyl substituents which merely cause general activation in the B ring without any localized effects such as those found in the A ring.

Formaldehyde reacts with tannins to produce polymerization through methylene bridge linkages at reactive positions on the flavonoid molecules, mainly the A rings. The reactive positions of the A rings are the position 6 of all the flavonoid units and positions 6 and 8 of the upper terminal flavonoid units. The A rings show reactivity toward formaldehyde comparable to that of resorcinol.[13] Assuming the reactivity of phenol to be 1 and that of resorcinol to be 10, the A rings have a reactivity of 8–9. However, because of their size and shape, the tannin molecules become immobile at a low level of condensation with formaldehyde, so that the available reactive sites are too far apart for further methylene bridge formation. The result is incomplete polymerization and therefore weakness. Bridging agents with longer molecules should be capable of bridging the distances that are too long for methylene bridges.

A variety of bridging agents were tried starting with resorcinol, resorcinol/ formaldehyde, and phenol/resorcinol/formaldehyde polymers of different types and ending with urea/formaldehyde and phenol/formaldehyde polymers:
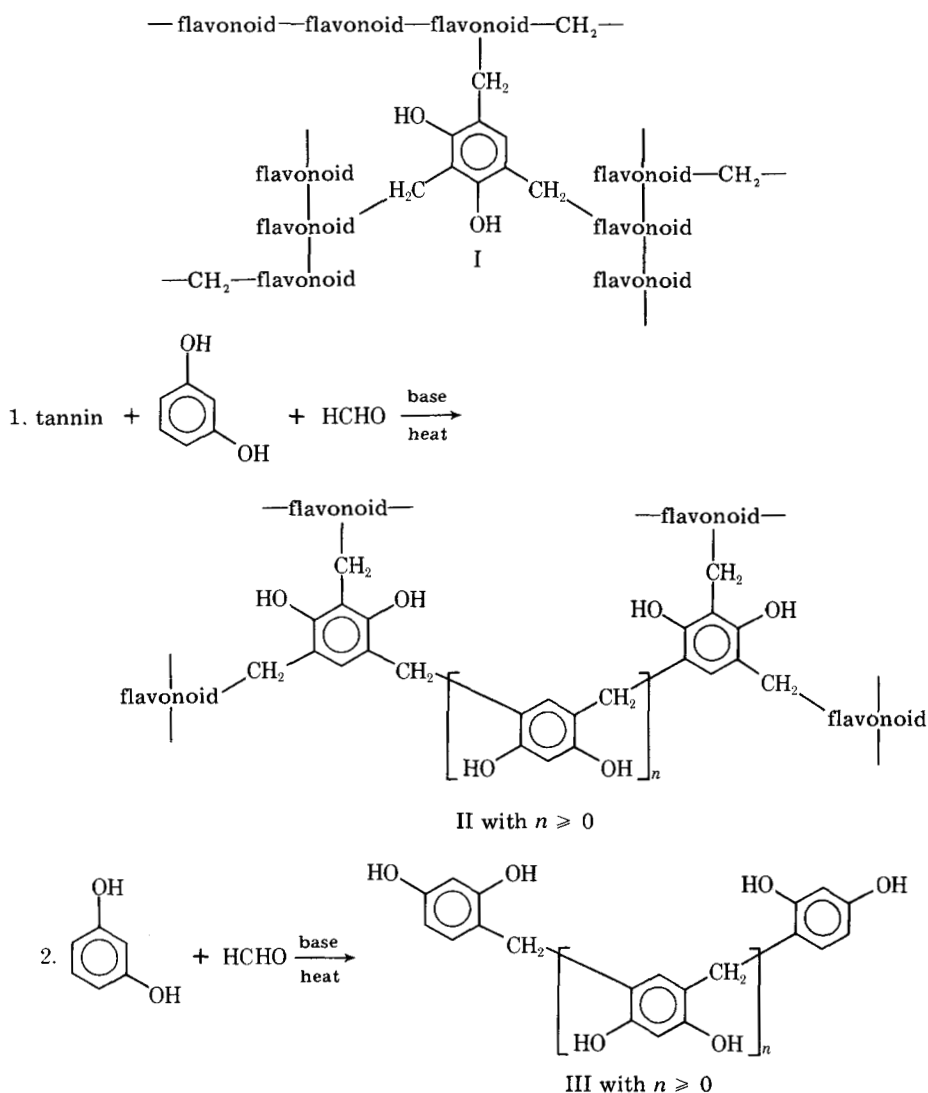
At first phenol was not considered because of the difference between its reactivity and that of the resorcinolic tannin A rings. The use of resorcinol as in cases (1) and (2) would require uneconomically high levels of resorcinol.

A phenol/formaldehyde resole with resorcinol grafted onto it might achieve

the same result.[6,14,15]   The following reactions should be feasible:

3. [structure] + HCHO $\xrightarrow[\text{heat}]{\text{base}}$ [structure]

IV with $n \geqslant 0$

IV + [structure] $\xrightarrow[\text{heat}]{\text{base}}$ [structure]

V with $n \geqslant 1$

V + lannin + HCHO $\xrightarrow[\text{heat}]{\text{base}}$

[structure]

VI with $n \geqslant 1$
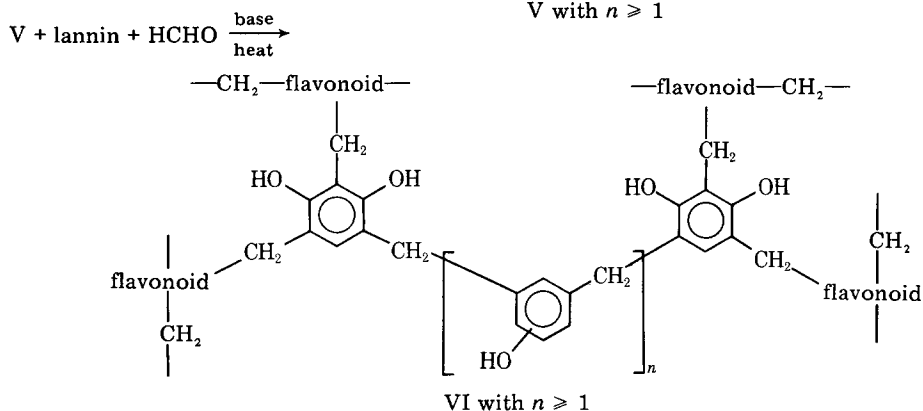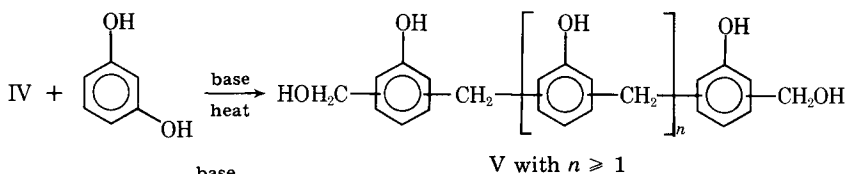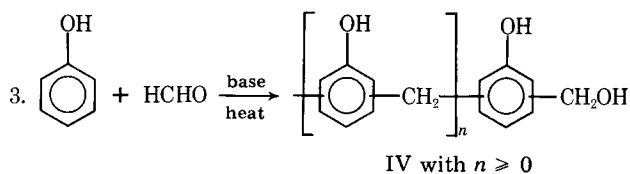
with VI very similar to II.

Another system to attain similar results is

4. [structure] + HCHO $\xrightarrow[\text{heat}]{\text{base}}$ [structure]

VII with $n \geqslant 0$

VII + tannin $\xrightarrow[\text{heat}]{\text{base}}$ [structure]

VIII with $n \geqslant 1$

VIII + HCHO $\xrightarrow[\text{heat}]{\text{base}}$

[structure]

IX with $n \geqslant 1$

Resin VIII is equivalent to resin V, the highly reactive crosslinking agent of resin V being the resorcinol and of resin VIII the tannin which, with an average polymer length of four to five flavonoid units, has more reactive points than resorcinol but is slightly less reactive due to steric reasons. In resin V the crosslinking of prereacted polymers is due to the formation of methylene bridges between the resorcinols of different phenolic polymers, between the resorcinols and the flavonoid A rings, and between flavonoid polymers only. In resin VIII, instead, the crosslinking of the prereacted polymers is due to the formation of methylene bridges between flavonoid units of different flavonoid/phenol/formaldehyde copolymers.

Another polymer capable of attaining similar results is a urea/formaldehyde resin; the reactions involved are probably the following:

$$5. \quad \text{tannin} + O{=}C\begin{array}{c}NR_2\\[4pt] NR_2\end{array} + HCHO \xrightarrow[\text{heat}]{\text{base}} \quad$$

with R = —H, —CH$_2$OH

flavonoid—CH$_2$—N$\overset{\overset{\displaystyle O}{\|}}{\underset{\displaystyle CH_2}{C}}$N—CH$_2$—flavonoid
polymer   polymer

flavonoid flavonoid
polymer polymer

X

The lack of resistance to water shown by urea/formaldehyde resins limits the amounts that can be added to the tannin. Urea/formaldehyde resins are not resistant to water attack and are classified as interior adhesives. The formation of a copolymer with the tannin will still not eliminate the —CH$_2$—NH— bonds easily hydrolyzable by water, and consequently increasing the amount of urea/formaldehyde resin will also weaken the water resistance of the copolymer.

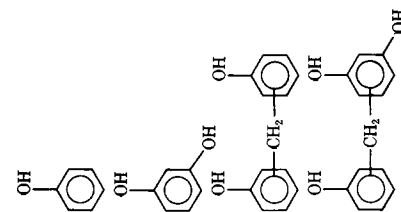6. Chemical species of lower reactivity toward formaldehyde than the flavonoid A rings can be used, assuming that, once a few methylene bridges between A rings are formed and the structure of the tannin/formaldehyde resin is practically immobile, these low-reactivity species occluded in the tannin/formaldehyde network can react with methylol groups already present on the flavonoid units, bridging gaps that are too wide to be filled by a single methylene bridge. A stable phenol/formaldehyde polymer (resin XI) containing no methylol groups can be mixed with the tannin and formaldehyde for this purpose. With this system the phenol/formaldehyde resin reacts with the flavonoid's methylol groups only after the methylene bridges have been formed, whereas in the previous systems the reaction of the phenol/formaldehyde and phenol/resorcinol/formaldehyde resins with flavonoid methylol groups takes place previously or simultaneously to the formation of tannin/tannin methylene bridges.

INCREASE OF ELASTICITY OF THE TANNIN/ FORMALDEHYDE POLYMER

7. Furfural, which is used to plasticize phenol/formaldehyde resins for foundry core binders, can be mixed with tannin and formaldehyde to obtain a tannin/furfural/formaldehyde copolymer of decreased brittleness,[6] improving the distribution of stress forces on the glueline and overcoming weakness due to stress concentration.
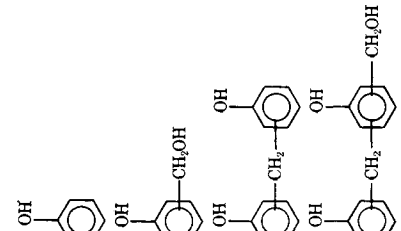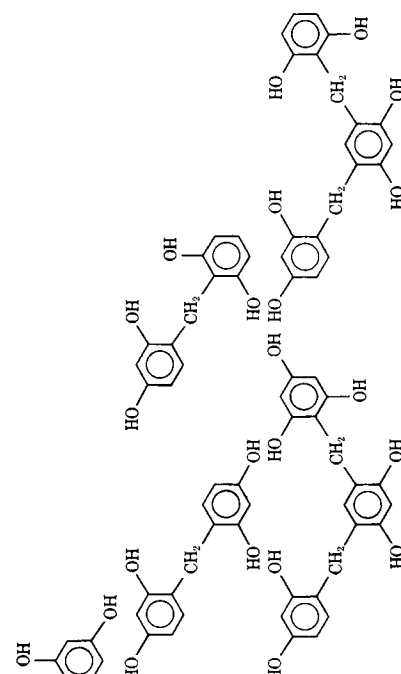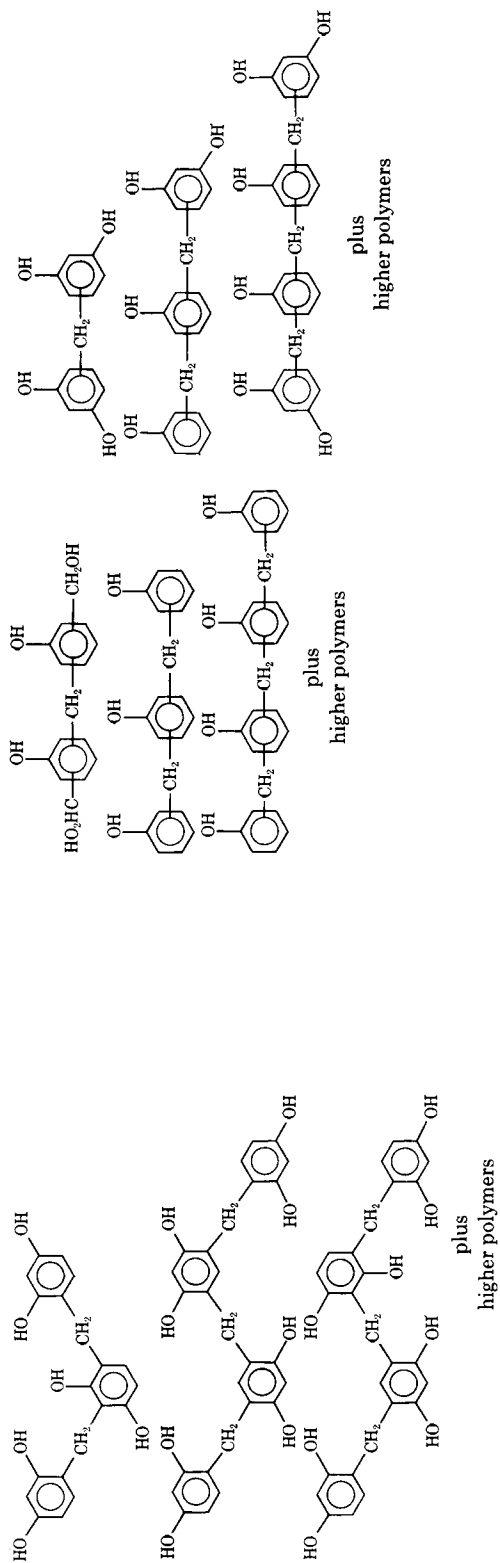
TABLE I

Characterization of Isolated Resin Fractions

Resorcinol:formaldehyde molar ratio 7:2	Phenol:formaldehyde molar ratio 1:1.02	Phenol:resorcinol:formaldehyde molar ratio First reflux 5:0:5 Second reflux { 5:2:5 8:2:5
Resin III	Resin IV and resin VII	Resin V and resin VIII

plus
higher polymers

plus
higher polymers

plus
higher polymers

EXPERIMENTAL

Resin Preparation

Resin III. A mixture of 56.4 parts 99% resorcinol and 11.5 parts 38% form-aldehyde solution was prepared at 25°C, 18 parts of an 80/20 water/methanol mixture were added, and then 8.4 parts of a 40% aqueous sodium hydroxide solution were slowly added. The mix was brought to reflux (93°C) in 10 to 15 min and was held refluxing for 60 min, then cooled and stored. The resorcinol: formaldehyde molar ratio was 7:2.

Resin V. A mixture of 40.3 parts 100% phenol 2.5 parts sodium hydroxide 40% and 34.5 parts 38% formaldehyde solution was prepared by addition and the mix was brought to reflux (91°C) in 10 to 15 min and held refluxing for 60 min, then 18.8 parts 99% resorcinol were added while dropping the temperature to 68°C and 24.2 parts 100% phenol were added with the temperature dropping to 43°C. The mixture was brought again to reflux (93°C) in 10–15 min and held refluxing for 60 min, then cooled and stored. Other variations of this resin were prepared decreasing the time of the first refluxing period from 60–20 and 10 min and the time of the second refluxing period from 60–30, 15, and 2 min. In one case, after the second phenol addition, the mixture was heated to 57°C and maintained there for 30 min, eliminating the second reflux period (case 6, Table II). In another two cases, after the second phenol addition, the mixture was cooled and stored (case 5, Table II). The phenol:formaldehyde molar ratio of the first part of the reaction was 1:1.02: the molar ratio after resorcinol addition is phenol:resorcinol:formaldehyde 5:2:5. The total phenol:resorcinol:formal-dehyde molar ratio is 8:2:5.

Resin VIII. A mixture of 148.0 parts 100% phenol and 126 parts 38% form-aldehyde solution was prepared at 25°C, 11.0 parts 40% aqueous sodium hydroxide solution were slowly added, and the mix was brought to reflux (93°C) in 10–15 min and held refluxing for 60 min. This mixture, still hot, was immediately added to 5182 parts of a 55% aqueous solution of wattle extract already at 93°C and containing 167 parts 40% sodium hydroxide solution and 7.5 parts of a commercial defoamer. The final mixture was maintained at 93°C for 60 min, cooled, and stored. The phenol:formaldehyde molar ratio was 1:1.03.

Resin XI. A mixture of 94 parts 100% phenol and 20.3 parts 38% formalde-hyde solution was prepared at 25°C, 9.6 parts 40% aqueous sodium hydroxide solution were added, and the mixture was brought to reflux (92°C) in 10–15 min, was refluxed for 90 minutes, cooled, and stored. The phenol:formaldehyde molar ratio was 1:0.25. To check the validity of the hypothesis discussed in the in-troduction and to see if phenol not prereacted with formaldehyde can contribute, in the presence of resorcinol, to improve tannins as adhesives for exterior ply-wood, the following mixtures were prepared:

Resin XII. A mixture of 64.5 parts 100% phenol, 31 parts water, 3.5 parts methanol, and 18.8 parts 99% resorcinol was prepared at 25°C, and 2.75 parts 40% aqueous sodium hydroxide solution were added. No formaldehyde was added.

Resin XIII. A mixture of 64.5 parts 100% phenol, 18.8 parts 99% resorcinol, and 11.5 parts 38% formaldehyde solution was prepared at 25°C, 2.75 parts 40% aqueous sodium hydroxide solution were slowly added, and the mixture was brought to reflux (93°C) in 10–15 min, was held refluxing for 60 min, cooled, and stored.

TABLE II
Adhesive 3, First and Second Refluxing Period

Panel no.	First reflux, min	Second reflux, min	Parts of liquid phenolic resin	Parts of solid wattle extract	pH	Pressing time, min	Species	Veneer moisture, %	OAT, hr	CAT, hr	Knife test rating Dry Outer	Dry Inner	24-hr cold soak Outer	24-hr cold soak Inner	6-hr boil Outer	6-hr boil Inner
1	60	60	10	100	6.5	6	Okoumé	6	—	5	9	8	8	9	9	8
2	60	30	10	100	6.5	6	Okoumé	6	—	5	9	8	9	9	9	9
3	60	15	10	100	6.5	6	Okoumé	6	—	5	9	8	9	8	9	8
4	60	2	10	100	6.5	6	Okoumé	6	—	5	9	8	9	8	9	8
5	60	—	10	100	6.5	6	Okoumé	6	—	5	9	8	9	8	9	8
6[a]	60	—	10	100	6.5	6	Okoumé	6	—	5	8	8	9	9	9	8
7	20	2	10	100	6.5	6	Okoumé	6	—	5	7	6	7	6	9	6
8	10	2	10	100	6.5	6	Okoumé	6	—	5	5	5	6	5	8	4
9	10	—	10	100	6.5	6	Okoumé	6	—	5	8	5	8	5	7	5

[a] 30 min at 57°C.

CHARACTERIZATION OF ISOLATED RESIN FRACTIONS

Three of the resins prepared were acidified with trichloroacetic acid and separated by thin-layer chromatography (TLC) on kieselgel No. PF 254 using a 70:30 benzene:acetone solvent for resin III and a 50:50 benzene:acetone solvent for all the other resins. The fractions separated by TLC were then scraped off the plates, washed with acetone, and then dried on a rotary evaporator, and the residue was analyzed by mass spectrometry. Resin III was also separated by column chromatography using a 50:50 benzene:acetone solvent on 60-mesh silica gel, and the different fractions obtained were analyzed by mass spectrometry and NMR, methylated with dimethyl sulfate, and then reanalyzed by mass spectrometry and NMR. The species formed in the variations of resin V were compared by TLC on kieselgel No. PF 254 using a 50:50 benzene:acetone solvent. The different species isolated and identified in the cases examined are shown in Table I.

PREPARATION OF GLUE MIXES

The glue mixes were prepared by mixing the components, by parts, shown in Table III. Enough of a 40% sodium hydroxide solution was added to the glue mixes, before the addition of paraformaldehyde, to reach a pH of 6.5 or 7.4. Small amounts of water were added to obtain an initial viscosity of 2.5 to 3.0 Pa.s at 22°C (1 Pa·s = 10 poises). In the glue mix of adhesive 5 − 1, sufficient 40% sodium hydroxide solution or 10% orthophosphoric acid solution was added to reach pH 3.0, 4.9, and 6.5. Viscosity increases (potlife) at a constant temperature of 22°C in a water bath were measured with a Brookfield RVF viscometer every hour or more frequently, when necessary, for all the variations of adhesive 3 to verify that small variations of time during the refluxing periods do not give significant variations in the characteristics of the resin obtained. The viscosity curves of all the variations of adhesive 3 all fell in the zone shown in Figure 1, where the viscosity curve of a simple tannin/formaldehyde mix in similar conditions is also shown.

TABLE III

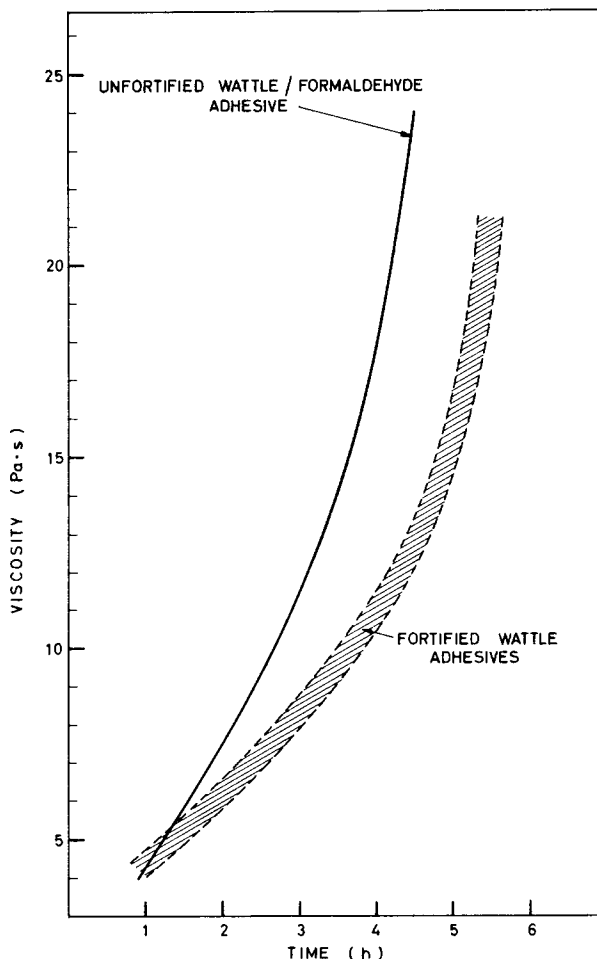|	Adhesive 1	Adhesives 2, 3, 4 + 6	Adhesive 5 − 1	Adhesives 5 + 7
Wattle extract powder	100.0	100.0	100.0	100.0
Defoamer	0.2	0.5	0.5	0.5
Water	72.0	90.0	110.0	100.0
Resorcinol	1.6	—	—	—
Phenolic fortifiers, liquid	—	as shown in Tables	—	—
U/F fortifier, solids	—	—	12.5	5.0
Furfural	—	—	—	10.0
96% paraformaldehyde, 180 mesh	14.0	14.0	14.0	17.0
Coconut shell flour, 200 mesh	20.0	21.0	18.0	22.0

Fig. 1. Potlife at 22°C. *1 Pa·s = 10 poises.

MANUFACTURE OF PLYWOOD PANELS

Duplicate plywood panels were prepared using different wood species under the following conditions: press temperature, 125°C; pressure, 1.37 MPa (1 MPa = 145 psi); pressing time, 2, 2½, 3, 3½, 4, 5, 6 min; veneer species, Okoume, Obeche, Sapele; % veneer moisture, 6, 8, 10, 12, 15; prepressing, 10 min at 0.49 MPa; open assembly time, 5, 12, 24 hr; closed assembly time, 5, 12, 24, 48 hr; glue spread, 180 g/m^2 s.g.l. (1 g/m^2 s.g.l. = 0.41 lb/MDGL); panel construction, 5 ply, each 1 mm thick; panel size, 30 × 30 cm.

Long assembly times are normal practice in the local plywood industry, and this was the reason why they were used. The performance of the adhesives is the same when very short assembly times are used.

TESTING

After manufacture the plywood panels were hot-stacked overnight in an insulated box, then trimmed, and cut into four 12.5 × 12.5-cm squares. Three squares for each of the duplicate panels were used to knife test the panels, one dry, one after 24 hr of cold water soaking, and one after 6 hr of boiling.

The knife test was evaluated in terms of British Standard BS 1088-1957 in which a rating from 0 to 10 is assigned, 0 indicating complete glue failure and 10, complete wood failure, and stating that no glueline shall have an overall quality of less than 2 and the average value for all gluelines tested shall not be less than 5.[16]

The results of the knife test are given in Tables II and V.

DISCUSSION

Table I shows that the phenolic condensates isolated from the preparation reactions satisfy the hypotheses advanced in the introduction for resins III, IV, V, VII, and VIII and adhesives 2, 3, and 4.

The results of Table II show that in the preparation of resin III the resorcinol had reacted with the available formaldehyde and methylol groups before the start of the second reflux period, which consequently can be eliminated from the preparation without any effect on the performance of adhesive 3. Table II also shows that the first reflux period, which entails the formation of the phenol/formaldehyde polymer onto which resorcinol must be grafted, has, on the other hand, a bigger effect on the performance of adhesive (3), a reaction time of 60 minutes giving better results than 20 or 10 minutes; however, the results obtained by using shorter reaction times are still good.

The results of Table IV show that there is no difference in the performance of adhesive 3 when 10 parts or more of resins are used. The performance of the adhesive decreases sharply when less than 10 parts of resin III are used.

Table V shows that adhesive 5 + 7 performs well when tested dry, after cold water soaking and after boiling. Adhesive 5 − 1 gave good results on different wood species and at different pH, indicating that this formulation performs well over a wide range of pH. Table V also shows that these adhesives are able to give good results on different wood species.

The results show that adhesives 3 and 6 can tolerate closed assembly times of at least 48 hr and open assembly times of at least 24 hr and that pH 6.5 is more suitable than pH 7.5 for obtaining long assembly times. Adhesive 5 + 7 can tolerate closed and open assembly times of at least 24 hr. Adhesives 3, 6, and 5 + 7 can tolerate pressing times as fast as 2–2½ min for 5 × 1-mm-thick panels: adhesives 3 and 6 can tolerate up to 12% veneer moisture content while adhesive 5 + 7 can tolerate only up to 10%. On industrial scale, pressing times would be slightly longer and veneer moisture content tolerance slightly less than those obtained in the laboratory.

Table V shows also that phenol unreacted with formaldehyde does not improve the results and that resorcinol not prereacted with formaldehyde does not improve the performance of the adhesive as much as resorcinol/formaldehyde, or, better, phenol/resorcinol/formaldehyde polymers at a comparable resorcinol content. Resorcinol/formaldehyde polymers do not give the same improvement as phenol/resorcinol/formaldehyde polymers at a comparable resorcinol content, since the resorcinol is not fully utilized.

When mixed with the tannin, resins V, VIII, and XI show indefinite shelflife both in liquid and spray-dried forms as long as the paraformaldehyde is not added. Adhesives 5 + 7 and 5 − 1 consist of ingredients which are not prereacted and merely require mixing before use and have the added advantage of being

TABLE IV
Adhesive 3, Percentage of Phenolic Polymer

Panel no.	First reflux, min	Second reflux, min	Parts of liquid phenolic resin	Parts of solid wattle extract	pH	Pressing time, min	Species	Veneer moisture, %	OAT, hr	CAT, hr	Knife test rating					
											Dry		24-hr cold soak		6-hr boil	
											Outer	Inner	Outer	Inner	Outer	Inner
10	60	—	25.0	100	6.5	6	Okoumé	6	—	5	8	7	8	9	9	8
11	60	—	15.0	100	6.5	6	Okoumé	6	—	5	8	8	8	9	10	8
12	60	—	12.5	100	6.5	6	Okoumé	6	—	5	8	7	7	9	9	8
13	60	—	10.0	100	6.5	6	Okoumé	6	—	5	8	7	7	9	9	8
14	60	—	7.5	100	6.5	6	Okoumé	6	—	5	6	7	5	7	7	4
15	60	—	5.0	100	6.5	6	Okoumé	6	—	5	5	5	5	5	5	5
16	60	—	2.5	100	6.5	6	Okoumé	6	—	5	7	5	6	5	6	4
17	60	—	0.0	100	6.5	6	Okoumé	6	—	5	7	6	5	5	5	3

TABLE V
Tolerance of Adhesives to Different Pressing Conditions

Panel no.	Adhesive type	First reflux, min	Second reflux, min	Parts of fortifier[a]	Parts of solid wattle extract	pH	Pressing time, min	Species	Veneer moisture, %	OAT	CAT	Dry Outer	Dry Inner	24-hr cold soak Outer	24-hr cold soak Inner	6-hr boil Outer	6-hr boil Inner
18	4	60	—	10 P	100	6.5	6	Sapele	6	—	5	10	10	9	9	8	8
19	4	60	—	10 P	100	7.4	6	Sapele	6	—	5	10	10	10	10	10	8
20	6	90	—	10 P	100	6.5	6	Sapele	6	—	5	10	10	9	10	10	9
21	6	90	—	10 P	100	7.4	6	Sapele	6	—	5	10	10	10	10	8	9
22	5 + 7	—	—	5 U	100	6.5	6	Sapele	6	—	5	10	10	9	9	10	9
23	5 + 7	—	—	5 U	100	7.4	6	Sapele	6	—	5	10	10	10	9	8	8
24	3	60	—	10 P	100	6.5	6	Obeche	6	—	12	10	10	10	9	10	9
25	3	60	—	10 P	100	6.5	6	Obeche	6	—	24	10	10	10	10	10	9
26	3	60	—	10 P	100	6.5	6	Obeche	6	—	48	—	—	9	7	9	6
27	6	90	—	10 P	100	6.5	6	Obeche	6	—	12	10	9	10	9	10	9
28	6	90	—	10 P	100	6.5	6	Obeche	6	—	24	10	9	10	10	9	10
29	6	90	—	10 P	100	6.5	6	Obeche	6	—	48	—	—	7	5	5	5
30	5 + 7	—	—	5 U	100	6.5	6	Obeche	6	—	12	8	10	10	8	8	7
31	5 + 7	—	—	5 U	100	6.5	6	Obeche	6	—	24	10	10	9	8	5	8
32	6	90	—	10 P	100	6.5	6	Obeche	6	12	—	9	9	9	9	10	9
33	6	90	—	10 P	100	6.5	6	Obeche	6	24	—	10	9	10	9	10	8
34	5 + 7	—	—	5 U	100	6.5	6	Obeche	6	12	—	9	10	9	8	7	8

No.																			
35	5 + 7	—	—	—	5 U	—	100	6.5	6	Obeche	6	24	—	9	7	9	9	10	9
36	3	—	60	—	10 P	—	100	6.5	2.5	Obeche	6	—	5	9	8	9	9	9	9
37	6	—	90	—	10 P	—	100	6.5	2.5	Obeche	6	—	5	7	9	9	9	9	9
38	5 + 7	—	—	—	5 U	—	100	6.5	2.5	Obeche	6	—	5	9	8	8	8	9	8
39	3	—	60	—	10 P	—	100	6.5	4.5	Okoumé	6	—	5	8	9	9	9	9	9
40	3	—	60	—	10 P	—	100	6.5	4.5	Okoumé	12	—	5	6	8	8	8	8	8
41	3	—	60	—	10 P	—	100	6.5	4.5	Okoumé	15	—	5			blisters			
42	6	—	90	—	10 P	—	100	6.5	4.5	Okoumé	6	—	5	9	7	9	8	9	9
43	6	—	90	—	10 P	—	100	6.5	4.5	Okoumé	12	—	5	4	6	7	7	8	8
44	6	—	90	—	10 P	—	100	6.5	4.5	Okoumé	15	—	5			blisters			
45	5 + 7	—	—	—	5 U	—	100	6.5	4.5	Okoumé	6	—	5	8	8	9	10	9	10
46	5 + 7	—	—	—	5 U	—	100	6.5	4.5	Okoumé	10	—	5	7	7	7	9	9	10
47	5 + 7	—	—	—	5 U	—	100	6.5	4.5	Okoumé	12	—	5			blisters			
48	5 − 1	—	—	—	12.5 U	—	100	3.0	6	Obeche	6	—	3	9	10	9	10	10	10
49	5 − 1	—	—	—	12.5 U	—	100	4.9	6	Obeche	6	—	3	8	8	9	9	10	10
50	5 − 1	—	—	—	12.5 U	—	100	6.5	6	Obeche	6	—	3	8	8	8	10	10	9
51	Wattle + HCHO only	—	—	—	—	—	100	6.5	6	Okumé	6	—	5	5	5	4	5	6	6
52	1	—	—	—	1.6 R	—	100	6.5	6	Okoumé	6	—	5	5	6	5	7	5	7
53	1	—	—	—	4.0 R	—	100	6.5	6	Okoumé	6	—	5	7	7	7	7	7	7
54	3 – XII	—	—	—	10.0	—	100	6.5	6	Okoumé	6	—	5	5	7	6	7	5	7
55	3 – XIII	—	—	—	8.0	—	100	6.5	6	Okoumé	6	—	5	7	7	7	7	7	7
56	3 – XIII	—	—	—	21.0	—	100	6.5	6	Okoumé	6	—	5	8	8	9	9	9	8
57	2	—	—	—	2.7	—	100	6.5	6	Okoumé	6	—	5	7	8	7	8	8	7
58	2	—	—	—	6.7	—	100	6.5	6	Okoumé	6	—	5	9	8	9	8	9	8

a P = Phenolic resin, liquid; U = U/F resin, solid; R = resorcinol, solid.

easily prepared by the end user who does not want to prereact components. Figure 1 indicates that the pot-lives of the resins tested is more than satisfactory for plant application.

The knife test results of Tables II, IV, and V show that the adhesives prepared give weather- and boilproof plywood, are able to tolerate assembly times of at least up to 48 hr, require glue spreads comparable to those of commercial phenolic resins, require short pressing times, and tolerate veneer moisture contents of up to 10%–12%.

CONCLUSIONS

Improving the degree of polymerization of tannin/formaldehyde polymers resulted in better performing adhesives, which confirms that the early immobilization of the tannin/formaldehyde network by relatively few methylene bridges is the main cause of the brittleness and poor water performance of simple tannin/formaldehyde condensates, and not the high reactivity of the tannin toward formaldehyde, which in fact is an advantage, as can be observed by the very fast pressing times obtainable.

When comparing the results obtained with adhesives 2 and 3 with those obtained with adhesive 6, there are indications that low reactivity species contribute to the improvement of the degree of polymerization of tannin/formaldehyde condensates, which confirms one of the hypotheses advanced in the introduction.

Plasticization of the tannin/formaldehyde polymer result in better distribution of stress forces on the glueline, improving the performance of the adhesive. It must be kept in mind, though, that furfural is not only a plasticizer but also, in a limited way when coupled with formaldehyde, a bridging agent for gaps wider than those than can be filled by plain methylene bridges, and consequently it contributes also to the improvement of the degree of condensation.

The phenol–formaldehyde reactions used were kept short, firstly because a range of short-length phenolic polymers is more desirable than highly condensed ones for bridging gaps in the tannin/formaldehyde network, as highly condensed phenolic polymers would amount to a waste of phenol or resorcinol in these cases; and secondly because highly condensed phenolic resins are in most cases incompatible with wattle extract in the proportions wanted and give, when mixed with wattle extract, precipitates due to too much water present or to a very fast and partial reaction with the tannin itself.

In conclusion, it may be observed that these resins show qualities similar to those of commercial phenolic resins. In the Republic of South Africa a few plants are already using similar wattle-based adhesives because they are economically competitive with phenolic resins.

References

1. L. K. Dalton, *Austr. J. Appl. Sci.,* **I,** 54 (1950).

2. K. Horioka, E. Sugano, Y. Katsuzawa, and K. Hayashida, Synthesis of Tannin Resin Adhesives and Their Properties, IUFRO Conference on Wood Glueing, Madison, Wisconsin, September 1975.

3. E. Knowles and T. White, Tannin extracts as raw materials for the adhesives and resins industries, *Adhesives & Resins,* **2** (nos. 10 and 11), (1954).

4. N. J. L. Megson, *Phenolic Resins Chemistry,* Butterworth, London, 1958.

5. A. Pizzi and H. O. Scharfetter, CSIR Confidential Report, 1976.

6. A. Pizzi, unpublished data, 1976.

7. A. Pizzi, D. Ferreira, and D. G. Roux, CSIR Confidential Report, 1976.

8. K. F. Plomley, J. W. Gottstein, and W. E. Hillis, *Tannin-formaldehyde adhesives, CSIRO* (*Australia*) *For. Prod. Newsletter,* **No. 234,** 6 (1957).

9. K. F. Plomley, 1966, *Tannin-formaldehyde adhesives for wood,* CSIRO Div. For. Prod. Technol. Pap., no. 39.

10. K. F. Plomley, The Development of Wattle Tannin Formaldehyde Adhesives for Wood by CSIRO, FO/WCWBD/75, Doc. No. 13, 1974.

11. D. G. Roux, *Fractionation of Wattle Extract* (Wattle Tannin and Mimosa Extract), Leather Industries Research Institute, 1968, pp. 48–51.

12. D. G. Roux, *Composition of the Tannins of Wattle Extract,* 1968, pp 52–64.

13. D. G. Roux, private communication.

14. H. O. Scharfetter, *For. Prof. J.,* **25** (3), 30 (1975).

15. H. O. Scharfretter, unpublished data, 1975/76.

16. Specification for Plywood for Marine Craft, British Standard BS 1088, 1957, pp. 1–19.